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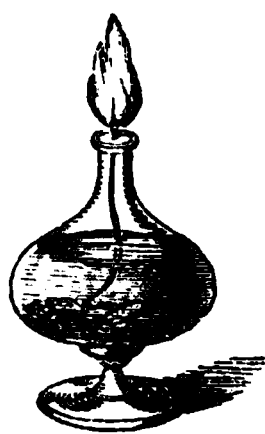
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W. & R. CHAMBERS
LONDON AND EDINBURGH

1871

193. f. 39.

‘Chemeia, alias Alchemeia, est ars corpora vel mixta, vel composita, vel aggregata etiam, in principia sua resolvendi, aut ex principiis in talia combinandi. Subjectum ejus sunt omnia mixta et composita, quæ resolubilia et combinabilia. Objectum est ipsa resolutio et combinatio, seu corruptio et generatio.’—STAHL, *Fundamenta Chemeiæ*.

AUTHOR'S PREFACE TO THE FIRST EDITION.

So many excellent text-books on Chemistry have been published within the last few years, that some apology seems necessary for the issue of another. It may be found in the fact that, admirable as are the extant treatises on the science, they are too extensive in their aim, too bulky, and too costly for a large class of students, who are anxious to acquire some knowledge of a branch of learning of which few can at the present day afford to be altogether ignorant.

The want of such a work has been felt so strongly by many, that the publishers of this volume have seen the necessity of meeting it in connection with their Educational Course, and, in compliance with their request, I have prepared the following treatise.

Its object is strictly elementary; its purpose being to introduce the student to a knowledge of the more important fundamental laws of Chemistry, and to make him familiar with the properties of the chief elementary substances and their more remarkable compounds. In conformity with this aim, much greater space has been devoted to the discussion of such subjects as the General Properties of Matter, Weight, Chemical Affinity, the Laws of Combining Proportion, the Atomic

Theory, Chemical Nomenclature, Chemical Notation, &c. than has been customary in works of the kind. Heat and Electricity have also been discussed in their chemical relations as fully as the limits of the work permitted, and quite as amply as beginners require.

In using this work, the teacher or pupil is recommended to read the first 108 pages with some care before proceeding further. The beginner must not expect to understand the introductory portions at once, but must go back from time to time to their study, when he will find them become more and more intelligible as he grows familiar with the properties of chemical substances explained in the later pages. On the other hand, some acquaintance with the contents of the preliminary chapters is essential to an intelligent study of the chemical elements, so that the earlier and the later chapters or sections must be studied alternately or together.

The Laws of Combining Proportion, and all that follows to the end of page 161, should be left unconsidered till the properties of oxygen, hydrogen, nitrogen, and their compounds, as detailed from pages 162 to 220, have been studied, after which the Laws of Combining Proportion and the Atomic Theory should be thoroughly learned.

A knowledge of Chemical Nomenclature and Notation cannot well be acquired too early; but it will depend greatly on the age, number, and capacity of the pupils, at what stage in their progress these subjects can best be introduced. This general direction, however, may be given: A portion of each lesson should be devoted to the study of the properties of the various elements and their compounds, with as full experimental illustration as circumstances permit, whilst another part of the lesson is devoted to such subjects as Chemical Nomenclature,

&c.; or the lessons may be alternated—an hour, for example, being devoted on one day to experiment and the exposition of phenomena, and on another to the explanation of laws and theories. In this way one set of lessons would begin at page 162, with Inorganic Chemistry, and the other at page 1 or 15, with the general principles of the science; whilst Heat and Electricity might be taken at intervals—for example, once a week—so as to introduce variety. The volume should supply materials for an hour's lesson daily for at least six months.

A single remark further seems called for. Greater importance is given to Chemical Notation in the following pages than in similar elementary works, and the immense majority of the chemical changes discussed are illustrated by symbols. Their employment has been objected to by some, as needlessly perplexing beginners. In this work, however, as far as possible, every chemical change has been explained in words as well as by symbols, so that those who choose may disregard the latter. It is not desirable, nevertheless, that this should be done; students, instead of disliking, prefer symbols, and rapidly acquire familiarity with their use, especially if gradually habituated to their employment (see note, page 135). In the present state of Chemistry, indeed, a student of the science is wronged if he is not made familiar with the chemical symbols, for they are employed by all chemists, and Organic Chemistry, instead of being simplified, would become more perplexing if symbols were exchanged for words.

EDITOR'S PREFACE TO THE PRESENT EDITION.

So much of Professor Wilson's original preface is applicable to the present time and the present edition, that the Editor feels that he need say very little in addition to explain the scope and intention of the treatise. He will be more than satisfied if the somewhat extensive alterations and additions, which the recent progress of Chemistry has rendered necessary, are found not to have deprived it of the simple and practical character which the author originally claimed for it.

The nomenclature has, in deference to the wishes of the Publishers, been brought into accordance with the system adopted by Professors Frankland and Williamson.

A few questions and exercises have been added at the end of the book, intended chiefly for those who are studying Chemistry by themselves.

October 1871.

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C H E M I S T R Y.

C H A P T E R I.

INTRODUCTION.

1. It would be of great advantage to the beginner in chemistry if it were possible to give a simple but sufficient definition of the nature of the science on the study of which he is about to enter, so that he might have some conception of the nature of the facts about which he is to be busied, and a certain preparatory acquaintance with the kind of knowledge with which chemistry deals.

2. Before, however, a single science can be properly defined, we must know not only it, but all other sciences perfectly, otherwise we may exclude from our definition something which it should have contained, or include something which in reality belongs to the definition of another science. As man, however, is not omniscient, he is unable to give perfect definitions of any of the sciences.

3. It is further to be remembered that the division of human knowledge into various branches, such as Chemistry, Physics, Physiology, Geology, and the like, is to a great extent made,

not because we can shew that a sharp line of demarcation separates each of these so-called sciences from all the rest, but because the limitation and feeble grasp of our faculties compel us to parcel out universal science, so as to restrict ourselves to departments of it, small enough to be investigated during the comparatively short life of a single individual.

4. Waiving, then, any attempt at logical definition, we may nevertheless endeavour to convey by description an idea of the nature and object of chemistry, sufficient to enable the pupil to begin his studies profitably.

5. The chemistry we are about to prosecute is that of the earth, our knowledge of the nature of the other bodies which exist in space being too limited to permit their chemistry being discussed at any length in this treatise.* Our globe, then, to which we restrict ourselves, may be considered as divided like a great kingdom among the students of the physical sciences. The astronomer, for example, explains its relations to the sun, the moon, and the other heavenly bodies. The geologist discusses the changes which have occurred on its greater masses since its creation, and dwells on the age, origin, and nature of rocks, fossils, volcanoes, mountains, valleys, rivers, seas, &c. The mineralogist, leaving to the geologist the question of the changes which the earth has undergone and the progress of life upon it from the earliest times, breaks down the great rocky masses into their proximate constituents, and examines the ores, soils, and spars, which by their union form the solid crust of the earth. The botanist investigates the forms, structures, and actions of dead and living plants; and the anatomist does the same in regard to animals. The physicist studies the effect of the various forms of natural Force, such as Heat, Light, and Electricity, upon matter in its different states of solid, liquid, and gas; he investigates the laws which determine the motion

* The recent important discoveries made with the aid of the spectroscope, while they belong rather to the domain of physics than that of chemistry, offer a striking illustration of the inter-dependence of the two branches of science, and of the light which each throws upon the other.

and equilibrium of bodies, besides much more which cannot here be enlarged upon. When these philosophers have exhausted all the resources of their respective sciences in explaining the physical characters of our planet, there still remains, among others, one most important question undecided, which the chemist comes upon the field to answer.

6. The problem which the chemist solves will be best understood by putting a question to certain of the philosophers to whom we have referred. The geologist, then, is asked to explain why coal and marble are so different from each other: Does each of them consist of one substance, and both of the same, or are they made up of many unlike ingredients; and if so, what are they? The mineralogist is requested to account for the difference in properties exhibited by the diamond and the ruby, and to say whether each consists of one kind of matter, or of several unlike kinds. A similar answer is required at the hands of the anatomist as to the cause of the difference in properties which distinguishes blood and milk from each other; and the physicist, in like manner, is applied to, to determine whether water and oil are, in nature, essence, or composition, in all respects identical, or differ totally as regards their component ingredients. To these questions no answers could be returned by any of the sciences to which we have referred. All of them would reply that it lay beyond the resources of their knowledge to furnish a solution of the problem. The science which solves it is chemistry, and the chemist may be represented as effecting its solution somewhat thus: He begins, as it were, by asking himself the question—Does our globe consist of but one kind of matter, or of several; and if of several kinds, of how many? He commences his practical work by arranging in classes all known substances according to their differences in external or sensible properties, such as weight, colour, odour, taste, &c. This preliminary labour is to a great extent done to his hands by his brethren the students of the other sciences, so that he receives, as it were, from the geologist and mineralogist, rocks and minerals, such as sandstone, granite, marble, opal, garnet,

chalcedony ; from the botanist and anatomist, woody fibre, sap, colouring matter, milk, blood, bone ; and from the physicist, oil, water, alcohol, and other liquids, besides solids and gases, with their sensible or physical characters accurately noted and recorded for his use.

7. The first point the chemist seeks to ascertain in reference to every substance, whether derived from the animal, vegetable, or mineral kingdom, is, does it consist of one kind, or of several kinds of matter ? The determination of this point enables him to make a primary division of all bodies into two great classes—simple and compound. Simple bodies consist of but one ingredient, as, for example, the various metals. Compound bodies of more than one constituent. Thus water contains two, sugar three, dry alum four, and pure white of egg six.

8. The processes which the chemist employs in order to discover whether bodies are simple or compound are various. The most common, perhaps, of all the agents which he brings to bear upon them is HEAT. Nearly every substance, for example, derived from plants and animals can be proved to be compound by simply heating it. Other bodies which resist the decomposing power of high temperatures, give way at once when exposed to the action of ELECTRICITY, and separate into their constituent parts. Many compounds which are indifferent both to heat and electricity are at once broken up by simply mixing them with other substances, and thus bringing into play the powerful agency of CHEMICAL AFFINITY. Thus oil of vitriol, or sulphuric acid, and hydrochloric acid, decompose with great rapidity the majority of mineral substances, owing to the fact that these acids have a greater tendency to combine with certain of the constituents of the mineral than with the rest. The compound is therefore broken up, those ingredients for which the acid has less affinity being left uncombined.

9. Again, LIGHT, especially sunlight, has a considerable power of effecting decomposition, and so have purely mechanical agencies, such as PRESSURE and violent CONCUSSION, to the

latter of which the ignition of a percussion cap is due. In a word, any agency which produces motion among the particles of a body, lessens their affinity for each other, and tends to shake them asunder.

10. Those may be regarded as the chief forces which the chemist employs for effecting decomposition, and they supply him with the means of distinguishing simple from compound bodies. Compound bodies may, accordingly, be defined to be those substances which, when subjected to heat, electricity, light, mechanical agencies, or chemical forces, applied singly, or taken, where that is possible, together, suffer resolution or decomposition into two or more ingredients, which cannot, by subjection to the same processes, be similarly decomposed. Simple bodies, on the other hand, are those substances which, so far as we can at present ascertain, resist the decomposing power of the forces referred to, and after the most protracted and repeated exposure to their influence, remain with every essential property altogether unchanged.

11. This exposure of substances to all known decomposing forces is spoken of by the chemist as their subjection to chemical *analysis*, a term derived from the Greek word *ἀνάλυσις*, and signifying the 'breaking up' or resolution of any complex substance into its primary constituents* or ultimate elements, or the process by which that resolution is effected.

12. As analysis is the foundation of all chemistry, though by no means sufficient of itself to constitute it a science, it is of the utmost importance that at the very outset the mode in which it is applied to furnish a basis for the science should be appreciated. To illustrate this, the following examples are given :

13. *Action of Heat.*—If a small quantity (about half a gramme, or less) of the substance called 'red oxide of mercury' (mercuric

* By 'primary constituents' are meant those substances which are obtained from a compound in the first step of analysis, and which may be themselves subsequently broken up into their ultimate constituents, which latter are called elements. Thus, in the case of marble (par. 14), quicklime and carbonic dioxide are its primary constituents; carbon, oxygen, and calcium are its ultimate elements.

oxide) be placed in a test tube and heated over a lamp, it will be observed to grow darker in colour, then to lessen in bulk, and finally to disappear entirely, while a mirror-like coating is formed on the cooler portions of the tube. This deposit, when touched with a glass rod, will run into bright globules of liquid mercury. Further, if a lighted match or taper be introduced into the tube, it will burn more brightly than in the air, shewing that some peculiar gas has been evolved from the substance. This gas, when further examined, would be found to be identical in properties with a gas called oxygen. Moreover, the weight of the oxygen, together with that of the mercury obtained, would be found to be exactly equal to the weight of the red oxide of mercury originally taken; and it has been found impossible, with our present means, to break up either the oxygen or the mercury into simpler substances. We therefore infer that the 'red oxide of mercury' is composed of two, and only two, dissimilar substances, oxygen and mercury, which are elements.

14. Again, a piece of marble, or limestone, presents no characters of colour, weight, or the like, by the mere inspection of which we can tell whether it consists of one or of several ingredients. We know, accordingly, that for ages it was looked upon as a simple substance, and called, with a multitude of others, earth. If a piece of marble, however, be strongly heated, as limestone is every day in our lime-kilns, it is decomposed or analysed into two totally unlike substances. The one of these is the familiar body quicklime: the other is a gas which, when it was first observed as derived in this way from marble, was called fixed air, because it has previously been in a state of fixation in the solid limestone; it is now called carbonic dioxide. Marble, then, is composed of at least two substances, lime and carbonic dioxide; but are these simple bodies, or may they not be made up of ingredients, as the marble was made up of them? This is a question which the further application of heat will not enable us to answer; since at the highest known temperatures quicklime and carbonic dioxide remain unchanged,

But by the employment of another agent, electricity, we can prove that lime consists of two substances, the one a brilliant yellow metal, called calcium; the other an invisible gas, called oxygen—the same, in fact, which we obtained from the mercuric oxide. But neither the calcium, nor, as we have already said, the oxygen, can by any process be resolved into two or more ingredients. The carbonic dioxide, in like manner, when another force, namely, chemical affinity, is brought to bear upon it, is decomposed. Carbon or charcoal may be obtained from it by heating in it certain metals, such as sodium or magnesium; and oxygen may be obtained from it by the action of living plants upon it. At this point our powers of decomposition stop; and we conclude that marble consists of three elementary bodies, calcium, carbon, and oxygen.

15. *Action of Electricity.*—The most familiar of all liquids, water, was for a very long time considered to be an elementary body. If, however, a powerful current of electricity be sent through it by dipping the poles of a galvanic battery (par. 243) into the trough containing it, we observe that gases are evolved from the surface of each pole (which should be made of platinum). If these gases are collected by holding over each pole a jar previously filled with water, and inverted, it will be found that only half as much gas is evolved from the positive pole as from the negative pole. The former, on examination, will be found to be oxygen; the latter will catch fire when a lighted taper is brought to the open mouth of the jar, and consists of a gas called hydrogen, which is considered to be an elementary body. And since the weight of the two gases is equal to the weight of the water decomposed, we infer that water is a compound consisting of two elements, and two only, namely, oxygen and hydrogen.

16. *Action of Light.*—This agent is scarcely used by the scientific chemist for the purposes of analysis, but one application of it has recently become of great importance. The whole art of photography depends upon the action of light in decomposing compounds containing silver.

17. *Action of Chemical Affinity.*—If some fragments of marble are placed in a glass, and some hydrochloric acid (hydric chloride) is poured over them, a violent effervescence takes place, owing to the evolution of a gas which may be proved to be carbonic dioxide. The marble has, in fact, been decomposed; the carbonic dioxide has been given off, while the elements of quicklime have united with the constituents of the acid to form water and a substance called calcic chloride.

18. Again, if a small piece of the metal sodium, an element which has a great affinity for oxygen, be placed upon the surface of water in a dish, a gas is evolved which burns when a lighted taper is brought near it, and possesses all the other properties of hydrogen. The sodium has decomposed the water, and by suitable means the whole of the hydrogen can be eliminated from water by the action of sodium, and a compound obtained, consisting solely of sodium and oxygen.

19. It is obvious that, when chemical affinity is employed as an agent of decomposition, one experiment is not sufficient to isolate all the elements of a compound, since some of them unite with the substance taken to effect the decomposition. For instance, in the last-mentioned case, the oxygen is not isolated, but enters into combination with the sodium. In order to obtain the oxygen, we must have recourse to a substance which has a greater affinity for hydrogen than for oxygen. Such a substance is the element chlorine. When a mixture of chlorine and steam is passed through a red-hot tube, the chlorine unites with the hydrogen, while the oxygen passes on in a free condition.

20. In the way thus illustrated, the chemist proceeds, subjecting all substances to his analytical processes; and whenever he comes to one which does not admit of analysis, he sets it apart, and calls it a *simple* or *elementary body*. In the present state of our knowledge, we count sixty-three bodies as simple, elementary, or not susceptible of analysis. The metals are all simple bodies. Fifteen substances which are not metallic belong also to this class.

21. Out of sixty-three elements, then, the thousands of chemical compounds known to us are made up. There is no body which contains them all, or even a majority of them. The greater number of substances contain a very few, and consist of only two, three, four, five, or six ingredients. Some of the simple bodies, moreover, form a much greater number of compounds than others. Certain of them, indeed, occur only in very small quantity in the globe, as constituents of rare minerals.

22. The sixty-three bodies referred to, which cannot be analysed, will hereafter be spoken of throughout this work as the Chemical Elements, or elementary bodies. They bear the same relation to the various compound substances which belong to the animal, vegetable, and mineral kingdoms, as the letters of the alphabet do to the words written in the language which they make up. Thus nearly every English word is a compound of two or more letters, into which it can be grammatically analysed. The twenty-six letters themselves, however, admit of no analysis, but are the primary symbols out of which the language is constructed. Certain of these letters occur much more frequently in words than others; thus one or more vowels are found in nearly every part of speech, whilst the letter Z enters into the composition of very few terms. The chemical elements may thus be called the alphabet of chemistry as a science, and the different compound bodies correspond to the words which are made up of the alphabetical letters.* Thus water is like a word of two letters, marble like one of three, alum of four, white of egg of six. In the following page we give a list of the chemical elements, to which we shall return again :

* It may be further remarked, as an extension of this analogy, that, just as the letters of the alphabet have in a few cases only, such as the vowels *a*, *i*, *o*, any verbal significance when uncombined, so it is believed that the chemical elements do not, as a rule, exist in the free state, but only in combination; that, for instance, the smallest particle of the gas hydrogen consists of a particle of the element hydrogen united with another similar particle of itself.

TABLE OF ELEMENTARY SUBSTANCES.

| | | |
|--------------------|----------------------------|----------------------------|
| Aluminum | Indium | Rubidium |
| Antimony (Stibium) | Iodine | Ruthenium |
| Arsenic | Iridium | Selenium |
| Barium | Iron (Ferrum) | Silicium or Silicon |
| Bismuth | Lanthanum | Silver (Argentum) |
| Boron | Lead (Plumbum) | Sodium (Natrium) |
| Bromine | Lithium | Strontium |
| Cadmium | Magnesium | Sulphur |
| Cæsium | Manganese | Tantalum or Colum- bium |
| Calcium | Mercury (Hydrar- gyrus) | Tellurium |
| Carbon | Molybdenum | Terbium (?) |
| Cerium | Nickel | Thallium |
| Chlorine | Niobium | Thorium |
| Chromium | Nitrogen | Tin (Stannum) |
| Cobalt | Osmium | Titanium |
| Copper (Cuprum) | Oxygen | Tungsten (Wolfram) |
| Didymium | Palladium | Uranium |
| Erbium | Phosphorus | Vanadium |
| Fluorine | Platinum | Yttrium |
| Glucinum | Potassium (Kalium) | Zinc |
| Gold (Aurum) | Rhodium | Zirconium |
| Hydrogen | | |

23. Analysis, or the resolution of bodies into their simplest ingredients, however, constitutes but half of the characteristic work of the chemist. In the case of a language, we do not merely resolve words into their component letters, but we combine these letters, so as to form new words, such as were not in existence previously. Thus, by analysing the hieroglyphics on the Egyptian monuments into their simplest constituents, we have discovered the grammatical elements of what for centuries was a lost language. We employ the knowledge so attained in reading the Egyptian inscriptions; but we might, in addition, construct new words out of the hieroglyphics, such as no Egyptian ever saw or made use of. In like manner, the chemist does not content himself with merely analysing the compounds which nature presents ready formed to his hand, but determines, by his interference, the

production of new ones, such as did not exist in the world till he effected their formation. Chloroform, for example, affords a striking illustration of a chemical substance which, so far as we know, occurs nowhere ready formed on the globe, but which has been called into existence by human interference within the last few years. It is not to be forgotten, however, that man has no real power of creating chemical compounds. He may bring together two elements which never met till he mingled them; but the combination which occurs between them is not effected by him, but results from the action of certain properties which the Author of all things has conferred upon these elements. It is only, therefore, in a secondary and subordinate sense that the chemist creates. The importance, however, of his office in this respect is not on that account to be overlooked. Few of our more valuable medicines, dyes, pigments, and other substances largely employed in the useful arts, are found native. The greater number of them must be prepared by complicated processes from what may be called the raw material, which alone is furnished by nature. Glass, for example, and soap, are in one sense artificial compounds, for they occur nowhere native; but in another are quite natural combinations, for had there not existed laws of nature determining their production, man could never have caused their formation.

24. This creation of new compounds by the union of their elements is called their production by chemical *synthesis* (from the Greek *σύνθεσις*), a term which stands exactly contrasted in meaning with *analysis*, signifying the placing together or union of bodies previously uncombined. Such combination may be effected by means of the same agents as are employed in analysis. Thus, we have seen that by the action of heat mercuric oxide is decomposed into mercury and oxygen. But if mercury is heated to a slightly lower temperature (just below its boiling-point) in contact with oxygen, the two substances slowly combine and form mercuric oxide. Again, if we take the two gases, oxygen and hydrogen, mixed in the proportions

in which they were obtained from water, and apply heat to them; they unite with explosion and reproduce water.

25. The action of electricity in effecting combination is by no means so general as its decomposing powers. It is true that the union of oxygen and hydrogen may be determined by the electric spark, but in this, and in most other cases, the heat of the spark is the real agent. But when a stream of sparks is passed through a mixture of oxygen and another gas called nitrogen, a combination of the two substances is formed; and this must be due to electric action, since we know that heat alone will not produce the effect.

26. Light also will cause combination. If a mixture of equal volumes of hydrogen and chlorine gases is exposed to sunlight, the two bodies unite with violence, and hydrochloric acid (hydric chloride) is produced. And chlorine may be caused to unite with many other substances besides hydrogen, under the influence of light.

27. But the most common means of effecting combination is chemical affinity. Indeed, if two substances have no attraction for each other tending to make them combine, then heat, electricity, and light fail to effect their union. The illustrations which were given in par. 17 of analysis by chemical affinity are, in fact, also illustrations of chemical combination. As an example of combination unattended by decomposition, the following may be taken. If a flake of the element iodine is laid upon a piece of carefully dried phosphorus, the two almost instantly combine with evolution of considerable heat, and a scarlet substance, phosphoric iodide, is produced.

28. The chemist's labours, which are thus partly analytic, partly synthetic, may be considered as beginning with analysis. He prosecutes it till he has resolved the globe, and everything on it, into sixty-three primary constituents or elements. He then betakes himself to synthesis—turning round, as it were, and retracing his steps, so as to pass now from simplicity to complexity; and by mingling the elements in innumerable ways, creates an endless number of novel substances. These

in their turn he subjects to analysis, in order that he may discover their exact nature and composition ; and thus Analysis and Synthesis constantly alternate, and frequently proceed together.

29. The prosecution of analysis and synthesis is in great part, however, only a means to an end. The new elements which the one, and the new compounds which the other brings to light, are each of them carefully studied as to all its properties. Thus the chemist examines, in regard to every substance, simple or compound, its shape, if it be a solid ; its specific gravity, whether it be solid, liquid, or gas ; its colour, odour, taste ; its melting, freezing, or boiling point ; its power to refract, reflect, and otherwise modify light ; its solubility in water and other liquids ; its action on living bodies ; the mode in which it affects other chemical substances ; the conditions essential to its entering into combination with these, and to its separation from them ; the proportion, by weight and volume, in which it combines with unlike bodies ; besides many other particulars. It is further to be observed that analysis and synthesis are not the only means by which the chemist extends his science. There are many other important methods of investigation, springing out of the relations of bodies to heat, light, electricity, magnetism, the forces which effect crystallisation, &c., which are constantly had recourse to for the extension of chemistry ; but it would be premature to enter at present on the discussion of these.

30. It will quite suffice for the beginner to regard chemistry as the science which takes cognisance of the fact that our globe, including its contents and inhabitants, does not consist of one, but of many species or kinds of matter ; and which investigates the differences that are presented by those kinds of matter, and the properties of the bodies formed by their union with each other. To return to our original illustration : if our globe consisted of but one chemical element—for example, were it a ball of lead, the astronomer could still discuss the problems of his science in relation to it ; the geologist, and

perhaps the mineralogist, would have something to describe concerning it; the physicist would have still more to explain regarding it; but the chemist would have nothing to proclaim in reference to such a globe. For all the sensible characters of a mass of lead, considered alone, fall under the notice of the philosophers previously referred to, who would leave nothing undescribed for the chemist to record. His characteristic office is to investigate the *differences* which subsist between unlike kinds of matter; but if there were but one kind—namely, lead—in existence, there could be nothing different to admit of comparison with it; so that in a globe of but one element, there could be no work for the chemist to do. Two elements as constituents of a world—lead, for example, and sulphur—would permit our science to come into action; and its range would widen as the number of elements increased. Our existent chemistry is the exposition of the differences which subsist between sixty-three elements, and the record of all the properties and material relations of each of these elements, and of all its compounds.

. The word *Chemistry* is derived from the Greek *χημεία* (*chemeia*), which occurs for the first time in certain works of the eleventh century, and is used by their writers to signify the *art of making gold artificially*, so that it originally denoted what we now generally indicate by the word *Alchemy*—namely, the supposed art of transmuting the common metals into gold. The root of the word is exceedingly doubtful. Some derive it from *Ham*, the son of Noah, one of whose immediate descendants is said to have been the first chemist; others from *Chemia*, one of the ancient names of Egypt, in which chemistry is said to have originated; some deduce it from the Coptic root *chems*, obscure or secret; and others from the Greek *chymos*, a liquid or juice—the aqua-regia of the alchemists being the liquid *par excellence*. Several other derivations have been proposed; but all are very uncertain, and none of them throw any light on the modern meaning of the word.

CHAPTER II.

GENERAL PROPERTIES OF MATTER.

31. The general properties of matter are discussed in a separate volume of this series of works,* and therefore are not enlarged upon here. There are certain of them, however, which must be briefly referred to, on account of the frequency with which allusion is made to them in all chemical discussions.

32. The masses of matter (liquid, solid, and gaseous) which present themselves at the earth's surface are looked upon as made up of certain minute particles, which, being arranged together in close approximation, build up larger solids, as a massive edifice is constructed by placing a multitude of hewn stones or moulded bricks together. To make the comparison complete, we must suppose the component stones to be very small, and that the joints or spaces between them are invisible. A block of iron is thus represented as the aggregation of a multitude of minute particles of the metal, kept united to each other by the attraction of cohesion, as the attraction of magnetism enables a loadstone to hold in contact with it a piece of steel. In like manner a liquid or a gas, in which the particles move freely on each other, may be compared to a battalion of soldiers clad in uniform. If looked at from a considerable distance, such a body of men, when each is motionless, appears as one indivisible mass. If approached more nearly, it is seen to consist of a multitude of individuals standing close

* *Laws of Matter and Motion*, p. 2.

to each other. When the battalion begins to move, it becomes apparent that its alterations in shape, and its movements as a whole, are occasioned by each soldier of which it consists systematically changing his place. Liquids and gases are, as it were, battalions of small particles, each of which corresponds to the individual soldier; but these particles are so minute that we cannot get sight of them, or perceive the manner in which they determine the movements of the fluids they make up.

33. The term 'molecule' (from the Latin word *molecula*, a small body) is applied to such particles of matter—namely, to the smallest portions into which a body can be conceived to be divisible by mechanical means. It will be seen hereafter that, in most cases, these molecules may, by chemical means, be divided into smaller parts (the molecule of water, for instance, into oxygen and hydrogen); but in such a case, the original properties of the substance completely disappear.

34. The molecules of matter are constantly exposed to the influence of two opposing forces, which change the physical or mechanical condition of the masses which result from the aggregation of many particles. These counteracting forces are cohesion and heat; the former approximates the particles of bodies, and renders them more dense and solid, or diminishes their volume; the latter (speaking generally) separates the molecules from each other, lessens the density and solidity of the mass, and expands its bulk. These opposing forces, according to their relative intensity, determine three distinct states or conditions of matter—SOLID, LIQUID, and GAS. In one, the attraction of cohesion prevails over the repulsive power of heat. This is the state of SOLIDITY. In another, heat has quite overcome cohesion, and we have, as a consequence, the GASEOUS state of matter. In the third, the opposing forces are balanced, or nearly so, cohesion still prevailing to a certain extent, and the resulting condition is that of LIQUIDITY.

35. A solid is distinguished from a liquid and a gas by the fact that we cannot move one particle of it without moving the whole. In other words, the particles of a solid are bound

so firmly and so closely together, that they cannot, without considerable force, be made to glide over each other. A propelling force, accordingly, if directed against a single particle or limited portion of a solid, either produces no result, or, if effective, moves the entire mass. In liquids and gases, on the other hand, we can put in motion some of the particles, and leave the remainder at rest, or have one set of molecules moving in one direction, and another in an opposite, as we see daily illustrated by the currents passing in unlike directions, which influence bodies of gas and of liquid, such as the atmosphere and the ocean.

36. It thus appears that, in solids, cohesion is so predominant, that the particles have for the time lost all freedom of motion among themselves. If the solid, however, be exposed to heat, and is not liable to decomposition, its particles immediately begin to move away from each other, and expansion or enlargement of bulk occurs. When the heat is withdrawn, the cohesive attraction recovers its power, and the particles move together again. Thus a rod of iron lengthens when placed in a fire, and shortens again when withdrawn from it. In liquids, as already observed, cohesion manifests itself, though much less strikingly than in solids. Detached drops of water or quick-silver run together into larger globules, shewing that attraction is operating upon them; but the force of cohesion is so small, that the particles are free to move with little obstruction upon each other, so as to admit not only of a general movement of the liquid, but of partial, smaller motions among its molecules.

37. Upon the particles of a gas, cohesion has ceased to exert any power; they repel, instead of attracting each other, and when relieved from pressure, or raised in temperature, recede from each other to the utmost attainable limit. Gases, as well as liquids and solids, contract or diminish in volume when cooled, but not for the same reason as these do—namely, because the withdrawal of heat has allowed cohesion to come into play—but simply because the diminution of the temperature

of a gas lessens the mutual repulsive action of its molecules, so that they do not, under the same pressure, recede so far from each other.

38. The same substance often presents itself in all three conditions, according to the temperature at which we examine it. As an illustration of this, let a lump of ice be placed in a flask and gently heated over a lamp. We observe that the solid loses its well-defined form, and is gradually converted into a substance which moulds itself to the form of the flask which contains it, its particles moving freely past one another when the flask is shaken. The solid, ice, has been converted by the heat into the liquid, water. After a time, if the application of heat be continued, bubbles will appear in the liquid, rising through it and bursting as they reach its surface. These bubbles consist of water which, under the influence of heat, has assumed the state of gas. This invisible gaseous water, or steam, soon fills the flask, but, from the repulsive action among its molecules, is not retained within it, like the liquid, but issues from the mouth, becoming visible as it encounters the cooler air and resumes the liquid condition.

39. Again, if a cold plate is held in the current of steam, the liquid particles, into which the steam is converted, run together into larger drops of dew, as the force of cohesion asserts itself; and if these drops are exposed to the cold of a frosty night, they resume their original solid state.

40. During all these changes, the chemical nature of the water remains the same. It is true that its affinities are altered; that, for instance, the liquid water will combine with substances with which ice will not combine, and that steam enters into union with substances upon which water has little action. But ice, water, and steam are found to consist of the same elements, oxygen and hydrogen, united in the same proportion.

41. There are certain substances which do not pass at once from the solid to the liquid state, but assume an intermediate or *viscous* condition, in which the mobility of their particles is greater than that of solids, and less than that of perfect liquids.

Thus iron, when heated nearly to its melting-point, becomes of a soft pasty consistence. When in this condition, two pieces of it can be readily joined or welded together by pressure, so as to form one homogeneous piece of metal. Similarly, glass, when heated to redness becomes soft and plastic, and can be moulded like hot sealing-wax into any desired form. There are indications* that the boundary-line between liquids and gases is by no means strongly marked, and that these states are really continuous, a substance passing gradually, not abruptly, from the one state to the other.

42. The force of cohesion differs considerably in different solids. In the case of some substances, we are able to stretch the mass to a certain extent without entirely overcoming the bond which holds the particles together. When a body in this way admits of being drawn into fine wire, it is said to be 'ductile;' when it can be beaten out into thin leaves, it is said to be 'malleable.' Gold possesses both these properties in a high degree; it may be drawn into wire finer than a hair, and beaten into leaves $\frac{1}{250,000}$ th of an inch in thickness. On the other hand, bismuth and sulphur crumble into powder under the hammer, and are placed in the class of brittle substances.

43. Sometimes the attraction of cohesion allows the molecules to be separated or approximated to a certain extent, but brings them back to their former positions when the constraining force is removed, so that the substance regains its original form. When this is the case, the body is said to be elastic. Steel affords a good example of this, and glass (although usually ranked among brittle substances) is, when in thin laminæ or threads, one of the most elastic solids known. Liquids and gases are, so far as experiments go, perfectly elastic bodies.

44. While cohesion only acts through extremely small distances, the molecules of matter are subject to another attractive force which acts through distances indefinitely great. This is the force of gravity, and it is found to be so universal in its action, that we may (roughly, and apart from metaphysical

* See the experiments of Dr Andrewes, *Phil. Trans.*, 1869.

speculation) define matter to be that which is subject to the law of gravitation. This law is expressed as follows: EVERY MOLECULE OF MATTER ATTRACTS EVERY OTHER MOLECULE WITH A FORCE VARYING INVERSELY AS THE SQUARE OF THE DISTANCE BETWEEN THEM. Thus, if we place two substances at the distance of 1 foot from each other, we shall find that there is a certain amount of attraction between them, a force tending to make them approach one another. If we place them 2 feet apart, this attraction will be $\left(\frac{1}{2^2} =\right) \frac{1}{4}$ th of the former amount; at 3 feet distance, it will be $\left(\frac{1}{3^2} =\right) \frac{1}{9}$ th, and so on. The quantity of matter in a body, which is termed its *mass*, is determined by observing the effect of the force of gravity upon a certain volume of it.

45. A special instance of the effect of gravitation is the property of weight, which will be treated of in the next chapter.

CHAPTER III.

WEIGHTS—WEIGHTS AND MEASURES—SPECIFIC WEIGHT.

SECTION I. WEIGHT—WEIGHTS AND MEASURES.

46. The property of weight, which may be defined to be 'the pressure exerted by bodies towards the centre of the earth,' is one of the utmost importance to the chemist. In all his investigations, he sooner or later examines the weight of the substances with which he is dealing. If he is engaged in an analysis, he weighs the original substance and the substances he obtains from it, and thus ascertains the proportions in which the latter combine. If he is endeavouring to form new compounds, he is no less careful to weigh the substances which he causes to act upon each other, and the products of their union.

47. For this purpose he uses an instrument called a balance. This instrument is constructed on the same principles as a common pair of scales, while it differs from the latter in various details, in order that it may indicate with certainty and precision very small differences in the weight of the substances placed in the pans. The construction of a chemical balance is shewn in figure 1 (page 22). It consists essentially of a straight lever, which is free to move through a small arc round a point at its centre called the fulcrum. This lever or 'beam' is not usually a simple straight rod, but a framework of brass in the form of an acute rhomboid, AA, the object being to combine lightness with stiffness. The fulcrum is formed of a triangular bar of hard steel passing through the beam, the lower edge of which bar is

ground very sharp, and rests upon a perfectly flat polished plate of agate on each side of the beam. At the extremities of the beam, and at precisely equal distances from the centre, are similar steel knife-edges turned upwards, and so adjusted that a straight line drawn from one to the other would just touch the lower edge of the fulcrum. On these rest agate planes, from which the pans, B, C, are suspended. Thus, when the beam oscillates, a

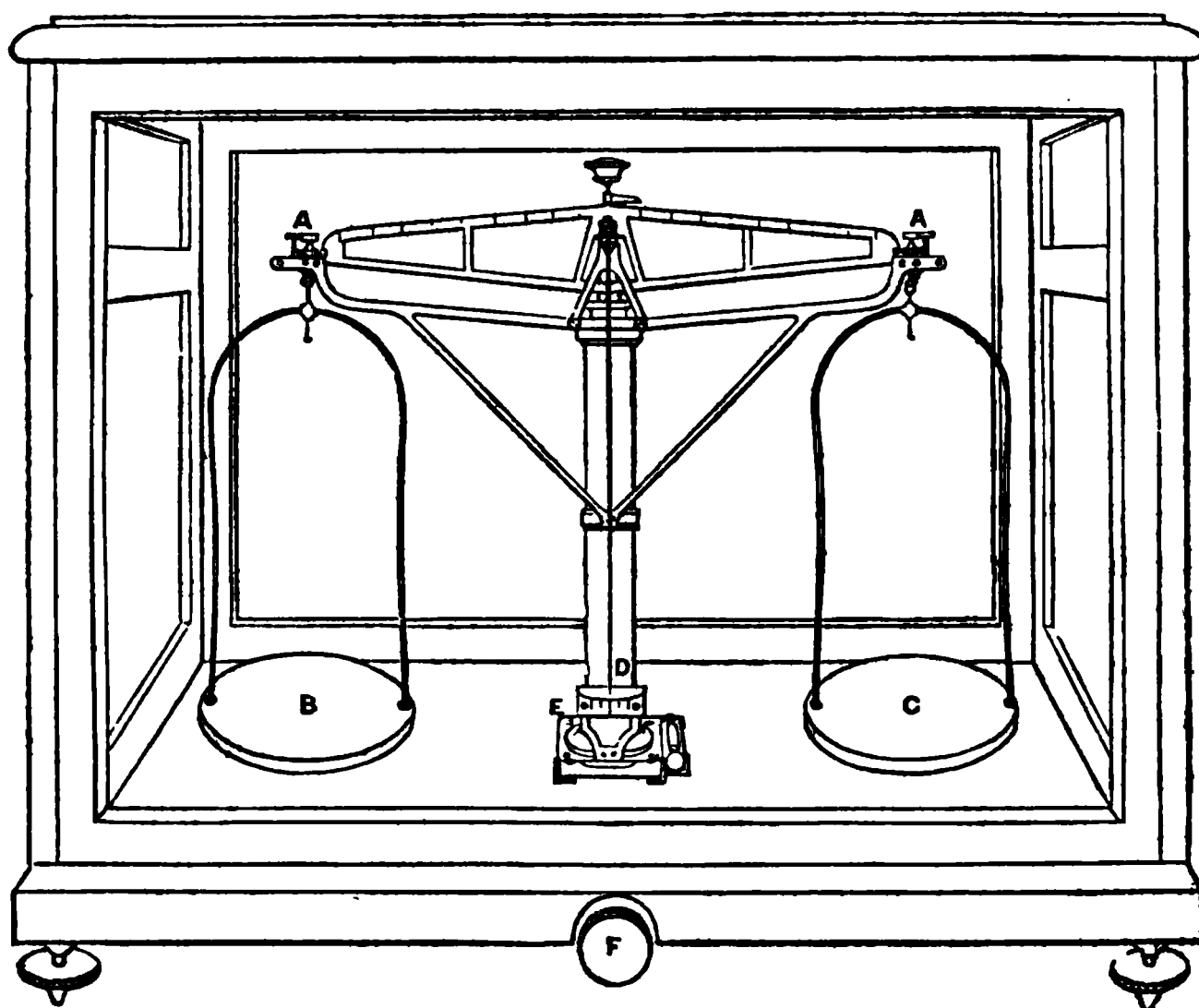


Fig. 1.

hard and extremely thin edge is moving upon a hard and perfectly flat surface, and the friction is reduced to a minimum ; while the distance between the fulcrum and the knife-edge at each extremity (in other words, the arms of the lever) is maintained equal, which would not be the case if the edges were of appreciable breadth.

48. The centre of gravity of the beam is so adjusted as to be very slightly below the fulcrum ; and hence, when the beam

with the pans suspended from it is left free to move, it should come to rest in a horizontal position. Since it would be difficult to judge of this position by the eye, a long steel pointer, D, is attached at right angles to the beam at its centre, reaching down to an ivory scale, E, and so adjusted that when the beam is horizontal the index points to the centre division of the scale. To prevent undue wear of the delicate knife-edges, there is an arrangement by which, on turning the milled head, F, the beam may be lifted out of contact with the agate plate, and the pans may be also supported independently of the beam. Finally, to protect the balance from currents of air and from dust, it is enclosed in a glass case, having doors at each end for introducing weights and substances to be weighed.

49. The operation of weighing a substance consists in balancing it against one or more pieces of matter, which we select as standards of comparison or units of weight. The selection of these is purely arbitrary, and every nation has had its own system of weights. There are, however, certain broad principles which should guide us in choosing a system for scientific work :

- (1.) The unit should be moderately small.
- (2.) It should bear a simple relation to the other measures, such as those of capacity and length.
- (3.) It should be such as to be easily recovered if lost or forgotten.
- (4.) The larger and smaller weights should be derived from the unit by the simplest possible system of multiplication and division.

50. There appears to be no system which fulfils these conditions so well as that which is called the metric system. This we shall proceed to describe, as it is rapidly superseding others in scientific work, and will be the only one employed in this book. It will be convenient to begin with the unit of length, since from it the other units are derived.

51. In the year 1791, the French government determined on the construction of a new system of weights and measures, the

base of which should be a definite portion (one forty-millionth) of the earth's circumference; and, as the first step, the size of the earth was to be measured with the utmost attainable accuracy. For this purpose, the distance between two places, Dunkirk and Barcelona, nearly on the same circle of longitude, was measured by the usual methods of surveying, and then, from the difference in latitude of the stations, it was known what fraction of the whole circumference this distance was. Thus, supposing that the difference in latitude, or the arc measured, was 10° (it was in fact $9^\circ 40'$), then, since the circle is divided into 360° , the measured length would be $\frac{1}{36}$ th of the whole circumference.

52. It would be impossible here to give the details of the measurement, although the subject is very interesting.* It is sufficient to say that, from the result of the measurement, a bar (a little longer than a yard) was prepared, which represented one forty-millionth of the earth's circumference, and was defined to be the standard of length, or METRE.† From this the other measures of length were derived by multiplying it and dividing it by 10, 100, 1000; the names of the larger measures, or multiples, being formed by prefixing to the word 'metre' a numeral derived from the Greek; the names of the smaller measures by similarly prefixing a numeral derived from the Latin. In this way the table given on the opposite page is constructed.

* This great scientific work was carried on in the midst of the horrors of the French Revolution; and the surveying-parties, headed by MM. Delambre and Mechain, were constantly in the greatest difficulties and dangers. An account will be found in the *Edinburgh Review*, vol. lxxvii.

† Recent investigations have shewn that this bar is not exactly what it was intended to be, but that it is .0000086 of a metre too short. It is, however, still taken as the standard. It seems certain that efforts to obtain a natural standard must fail, and that we must be content to copy an arbitrary standard.

Length.

| | |
|-------------------------------|----------------|
| Kilometre | = 1000 metres. |
| Hectometre | = 100 " |
| Decametre | = 10 " |
| METRE (m.) | = 1 metre. |
| Decimetre | = 0·1 " |
| Centimetre (cm.) | = 0·01 " |
| Millimetre (mm.) | = 0·001 " |

Volume.

| | |
|---|----------------|
| Kilolitre | = 1000 litres. |
| Hectolitre | = 100 " |
| Decalitre | = 10 " |
| LITRE | = 1 litre. |
| Decilitre | = 0·1 " |
| Centilitre | = 0·01 " |
| Millilitre (or cubic centimetre) (c. c.) | = 0·001 " |

Weight.

| | |
|---------------------------|-----------------|
| Kilogramme | = 1000 grammes. |
| Hectogramme | = 100 " |
| Decagramme | = 10 " |
| GRAMME (gm.) | = 1 gramme. |
| Decigramme | = 0·1 " |
| Centigramme | = 0·01 " |
| Milligramme | = 0·001 " |

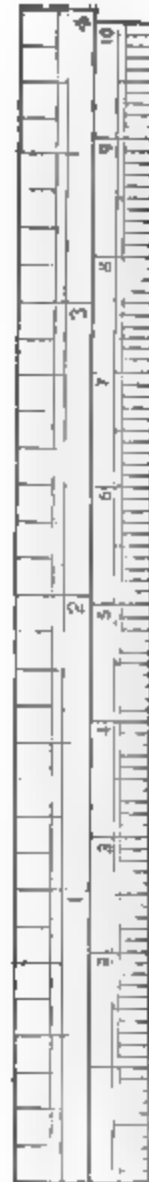


Fig. 2 represents a decimetre compared with a scale of English inches.

| | |
|-------------------------|-------------------|
| The metre | = 39·3708 inches. |
| The litre | = 1·76 pints. |
| The gramme | = 15·432 grains. |

53. From the unit of length, the unit of volume, or capacity, is simply derived. It is a cube, each side of which measures one decimetre, and is called a LITRE. The other measures are derived from it by multiplication and subdivision by 10, 100, 1000, precisely as the measures of length, and their names are formed on the same principle. A table of these measures is given on the previous page. It may be noted that, in chemical work, quantities smaller than the litre are usually expressed in cubic centimetres, instead of decilitres, &c. Thus, half a litre would be expressed (not as 5 decilitres, but) as 500 c.c.

54. We come lastly to the unit of weight, with which we are now more immediately concerned. It is called the GRAMME, and bears a simple relation to the other units, being the weight of one cubic centimetre of pure water at the temperature of 4° centigrade.* The other weights are multiples and subdivisions of the gramme, derived in the same way, and named on the same principle as those of the metre and litre. A table is given on the previous page.

55. The symmetry, simplicity, and general convenience of this system are obvious, and it is much to be hoped that it will come into universal use. As an example of its advantage may be taken the simple relation between the units of weight and volume, which enables us most readily to reduce quantities by weight into quantities by volume, and *vice versa*. Thus, a given volume of water, expressed in cubic centimetres, will weigh (neglecting the small correction for temperature) the same number of grammes; and if we were dealing with a substance twice as heavy as water, bulk for bulk, we could state, without further calculation, that a certain weight—for instance, 100 grms.—of it would measure 50 c.c. It is often convenient to apply this in practice when measuring-flasks are not at hand.

56. The operation of weighing is one which requires extreme care and undeviating method. Before beginning to work, it should be ascertained that the balance is in good order, that

* The significance of this particular temperature will be explained in the chapter on Heat (par. 103).

the beam swings freely, and comes to the horizontal position when it is lowered in its bearings by turning the milled head.* After again raising the beam, the substance to be weighed may be placed in one scale (preferably the left-hand one), and weights added one by one to the other scale, the beam being lowered by a turn of the milled head after each addition of weight, and raised again before another weight is placed in the scale. Nothing should be placed in, or taken out of, the scales while the balance is free to swing. The weights should be tried in a definite order, beginning from the largest, until it is found that, when the beam is lowered, the pointer remains at rest at the centre division of the arc, or at anyrate oscillates through an equal number of divisions on either side of the centre. When this is the case, the weights in each scale-pan are equal. It is remarkably easy to make mistakes in reckoning the small weights, and they should always be counted over twice—once in the scale-pan, and again as they are put away in the box—the result being written down *at once*. Since the platinum weights smaller than the centigramme are inconveniently minute, each arm of the beam in the best balances is divided into ten equal parts, and a small wire weight, called a rider, is used, which may be placed at varying distances along the beam. If this rider weighs 1 centigramme when at the end of the beam or in the pan, then, if placed midway between the centre and the end, it will be equivalent to a weight of half a centigramme in the pan; if placed at the first division, reckoned from the centre, it will weigh $\frac{1}{10}$ th of a centigramme, or 1 milligramme, and so on.

* A small vane-shaped piece of metal is usually placed just above the centre of the beam, by turning which in one direction or the other, the balance may be brought into equilibrium before use. But this should be sparingly used; and, before altering it, such remedies as dusting the scale-pans with a feather or soft brush should be tried.

SECTION II. SPECIFIC WEIGHT.

57. If we weigh in the balance one grm. of cork, and compare its size with the size of the gramme weight which counterbalances it, we shall find that the two equal weights of matter differ considerably in the space they occupy, in their bulk or volume. Similarly, if we take a piece of cork and cut it to the size of the gramme weight, and then ascertain its weight, we shall observe that the two equal bulks of matter differ considerably in weight.

58. It is this relation of bulk to weight which we have now to consider. In practice, it has been generally found most convenient to ascertain the comparative weight of equal bulks, rather than the comparative bulk of equal weights. Some one substance is selected as the standard with which equal bulks of other substances are compared as to weight. If the weight of a certain volume of this substance be assumed = 1, then the number expressing the weight of the same volume of any other substance is termed the 'specific gravity' of the latter. Thus, it is found that while 1 c.c. of water weighs 1 grm., 1 c.c. of mercury (at the same temperature) weighs 13.59 grm. The specific gravity of mercury is therefore said to be 13.59.

59. Specific gravity, then, may be shortly defined as 'the relative weight of equal volumes of different substances.' A preferable expression is 'density,' which, however, is usually, but unreasonably, restricted to gases. Water is universally accepted as the standard of comparison for liquids and solids, and air is commonly taken as the standard for gases and vapours. For the latter, however, chemical reasons would lead us to prefer hydrogen as the standard; and while in actual experiments we are almost compelled to accept air as our point of immediate reference, yet, having once for all determined accurately the density of hydrogen, a simple proportion sum

will enable us to express all other densities on the hydrogen scale.*

60. We shall now proceed to give examples of the methods of determining the specific gravity of matter in each of its three states, of gas, liquid, and solid.

61. *Gases.*—The mode of determining the density of a gas is very simple in principle, although, from the fact that gases weigh very little compared with the weight of the vessel containing them, considerable difficulties and uncertainties arise in practice. A large glass globe, provided with a stop-cock, is weighed when full of dry air, then thoroughly exhausted by a good air-pump, and again weighed. It will now, of course, weigh less than at first; and this weight, subtracted from the former weight, will give us the weight of the volume of air which the globe contains. It is then filled with the gas of which the density is required, and again weighed, care being taken that the height of the barometer and the temperature of the globe are the same as during the former weighing, or, at anyrate, that the changes in pressure and temperature are known.† The weight of the empty globe, subtracted from the weight of the globe full of gas, gives the weight of the gas which the globe contains. We have now ascertained all that is required—namely, the weights of equal volumes (the volume contained in the globe) of air and the gas under examination. Then, from the proportion,

$$\text{Weight of air} : \text{weight of gas} :: 1 : \text{density of gas},$$

we obtain the density sought for.

62. *Vapours.*—The above method is, of course, only applicable to gases which are permanent at ordinary temperatures. When we wish to ascertain the density of a vapour—that is, a body which requires a more or less elevated temperature to

* A table giving the densities of the more important substances will be found at the end of the book.

† For since, as will be hereafter shewn, gases change in volume under changed pressure and temperature, we should not otherwise be comparing strictly equal volumes of the two substances.

retain it in the gaseous state—we employ another method similar in principle, which was invented by the French chemist Dumas. A small globular flask is selected, and the neck drawn out to a fine tube, after which it is accurately weighed. Some of the substance of which the vapour density is required is introduced by warming the flask, and then dipping the end of the capillary neck into the liquid. As the air cools and contracts, some of the liquid will be forced up into the flask by the pressure of the external air. The flask is then lowered into a bath of oil or mercury, which is heated considerably above the boiling-



Fig. 3.

point of the liquid. The vapour formed gradually chases out all the air in the flask, and eventually we arrive at a point at which no more vapour issues from the neck, all the liquid having evaporated. The flask is now filled with the pure vapour of the substance; its neck is sealed by directing on it the flame of a blow-pipe, and the temperature of the bath, and pressure indicated by a barometer, are observed at the moment of closing the flask. When it is cool it is again weighed.

63. We have now two of the data required: (1.) the weight of the flask full of air; (2.) the weight of the flask full of the vapour. But we want further to know the weight of the empty flask. This we can obtain if we know the capacity of the globe in cubic centimetres, and the weight of 1 c.c. of air. The point of the neck is broken off under mercury, which rushes in and fills the flask, with the exception of the drop of liquid into which the vapour has condensed. When this has been replaced by mercury, the latter is carefully measured, and thus we learn the capacity of the flask. Suppose that this is 200 c.c. Then the weight of 200 c.c. of air, at the temperature of the room, subtracted from the original weight of the flask

full of air, will give the weight of the empty flask; and this latter weight, subtracted from the weight of the flask filled with the vapour, will give the weight of 200 c.c. of the vapour at the temperature at which the flask was sealed. We have then only to calculate the weight of 200 c.c. of air at the same temperature,* and we get the proportion:

Weight of air : weight of vapour :: 1 : density of vapour.

But, as has been said, it is preferable, for many reasons, to refer the density of the vapour to hydrogen as the standard. For this purpose, we must substitute, for the first term in the above proportion, the weight of the same volume of hydrogen at the given temperature.†

64. *Liquids*.—Since the problem is simply to ascertain the weight of a certain bulk of the liquid, and compare it with the weight of an equal bulk of water, we have only to take a vessel of any convenient size, the weight of which is known, and to determine its increase in weight, (1) when filled with water, (2) when filled with the given liquid, at the same temperature.

65. A convenient apparatus for the purpose consists of a small flask holding about 50 c.c., the neck of which is contracted in one part, and a mark made near the middle of the contracted portion.‡ This is carefully weighed, when clean and dry, and the weight recorded once for all in a book, or with a writing diamond on the flask itself. Pure distilled water is then poured in, until on bringing the neck of the flask, held truly vertical, to the level of the eye, the *lowest* part of the curve formed by the surface of the water just appears to touch the file mark. If too much water is added at first, the excess should be removed by a glass rod or strip of blotting-paper. The flask is now again weighed, and the difference between this and the original weight gives the weight of water taken. After being dried,

* For the method of making these calculations, see par. 106, note.

† For other methods of determining vapour densities, the student is referred to Greville Williams's *Chemical Manipulation*, or Cooke's *Chemical Physics*.

‡ Any narrow-necked flask or stoppered bottle will answer, and the mark may easily be made by a three-square file, a ring of paper being previously pasted round the neck, to guide the edge of the file.

the flask is filled up to the mark with the liquid the density of which is required, and the weight again taken. The difference between this and the original weight, is the weight of a volume of the liquid equal to that of the water.* Then, by the proportion :

Weight of water : weight of liquid :: 1 : density of liquid.

66. There is another method of taking the density of a liquid where only approximate accuracy is required—namely, by the use of an instrument called a hydrometer. This

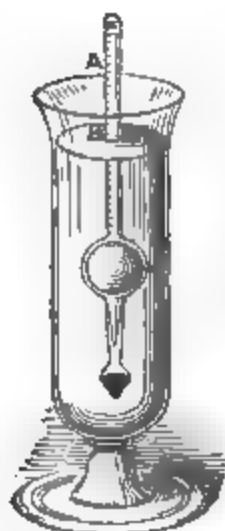


Fig. 4.

instrument is shewn, immersed in water, in fig. 4. It consists of a glass tube, having a bulb attached at one end, below which is a smaller bulb, partially filled with mercury, so as to cause the tube to swim upright in a liquid. Its use depends on the hydrostatic principle, that 'a body floating in a liquid displaces a volume of the liquid weighing as much as itself.' It will be seen, then, that if the hydrometer is weighted so as to sink to the point A in water, when it is placed in a liquid heavier than water it will not sink so far, since a smaller volume of the heavier liquid will correspond

to the weight of the hydrometer. For a similar reason, if it is placed in a lighter liquid it will sink further; and thus we may state generally that the amount of the stem submerged is inversely proportional to the density of the liquid. The stem is graduated by marking the points to which it sinks in liquids of known density, such as ether, water, and oil of vitriol, and (assuming the tube to be of the same size throughout) dividing the spaces between these points into any convenient number of parts. To find the density of an unknown liquid, the hydrometer is immersed in it, and the division which coincides with the surface of the

* The temperature of the liquid should not differ much from that of the water; otherwise, for the reason stated in speaking of gases, inaccuracies will arise.

liquid, as seen from below, gives, without any calculation, the density of the liquid. The temperature of the liquid must be noted, and should not differ much from the temperature at which the hydrometer was adjusted, which is usually marked on the instrument.

67. *Solids*.—It would be obviously difficult, in the case of solids, to obtain portions of water and of the solid exactly corresponding in size. But we can easily obtain the required data by taking advantage of the hydrostatic principle, that ‘a solid immersed in a liquid loses a weight equal to the weight of an equal volume of the liquid.’ All that is required, therefore, is, to weigh a piece of the solid in air, and then immerse it in water, and weigh it again in that position. For this purpose, a small wooden bridge is placed over one of the scale-pans, just high enough to allow the scale to move freely under it, and broad enough to support a vessel of water, such as a tumbler, sufficiently large to admit of the solid hanging in it without touching the sides. The substance is suspended in a noose of fine horse-hair or platinum wire from a hook, shewn in fig. 1, just under the end of the beam. Its weight in air is first ascertained, and then the vessel is carefully filled with pure water, so that the solid may be completely immersed. Any adhering bubbles of air must be removed by touching them with a wire or feather. The substance will now weigh less than before, and the weights must be re-adjusted until equilibrium is restored. If this latter weight be subtracted from the original weight of the substance, we obtain (as stated above) the weight of an equal volume of water. Then, by the proportion :

Wt. of equal vol. of water : wt. of substance in air : : 1 : density of substance.

In other words, divide the weight in air by the loss of weight in water, and the quotient will be the density of the substance.

68. In the case of a solid which is lighter than water, a modification of the above method is necessary. The substance is first weighed in air, and then attached to a solid, the weight of which in air and water has been determined, and which is

sufficiently heavy to sink it in water. Then the difference between the loss of weight of the heavy body alone when immersed in water, and that of the combination when similarly immersed, will be the weight of a volume of water equal to that of the light body. The density of the latter is then obtained by the rule given above.

69. Another case of frequent occurrence is the determination of the density of a substance which is soluble in water. It is then impossible to weigh it in water, but it must be weighed in a fluid which does not dissolve it, and the density of which is known. Then we have the following data :

(1.) The relative weights of equal bulks of the substance and of the liquid in which it was weighed.

(2.) The relative weights of equal bulks of the liquid and of water. Hence the weight of a volume of water equal to that of the substance is obtained by the following proportion :

$$\text{Density of the liquid : 1} :: \left\{ \begin{array}{l} \text{weight of the liquid dis-} \\ \text{placed by the substance} \end{array} \right\} : \left\{ \begin{array}{l} \text{weight of an equal} \\ \text{volume of water} \end{array} \right\}$$

and the density may then be found in the usual way.

70. The importance of the determination of densities scarcely needs illustration. The density of a gas, as will be seen, bears a simple relation to the proportion in which it enters into chemical combination, and is always appealed to in order to decide the weight of the molecule of the gas. The density of liquids containing alcohol is used in the excise to determine the amount of alcohol they contain. In mineralogy, again, the density of rocks and crystals is of great value in determining their nature. No one who could take the density of the substance would ever confound diamond with quartz or zircon, or gold with iron pyrites.

CHAPTER IV.

CRYSTALLISATION AND CRYSTALLOGRAPHY.

71. In a large number of substances, both simple and compound, the molecules shew a tendency to arrange themselves in regular geometrical forms which have generally plane surfaces, bounded by angles which are constant. These geometrical solids are termed *crystals*, and the process by which they are produced is called *crystallisation*. Crystallisation is generally determined by conferring fluidity upon the substance to be crystallised, so as to give its particles freedom of motion on each other, and then leaving the fluid undisturbed, so that the molecules may slowly return to the solid state.

72. A crystallisable body is either rendered fluid by heating it till it melts into a liquid, or sublimes as a vapour; or it may be dissolved in a liquid which is afterwards caused to evaporate slowly. Some substances, such as sulphur, can be crystallised in all the three ways—that is, by fusion, vaporisation, or solution; the greater number of the metals chiefly by fusion, the majority of salts and crystallisable organic bodies by solution. It is also possible, by decomposing a compound liquid or gas, to obtain one or more of its constituents crystallised. The metals, for example, are readily crystallised by decomposing their solutions slowly by galvanic currents; and various compound gases, when passed through red-hot tubes, deposit certain of their constituents as crystals. Uncrystalline solids also, such as malleable iron, in certain circumstances, have a crystalline

structure developed in them, without becoming in the slightest degree fluid.

73. The same substance often crystallises in a great variety of shapes; but when these are carefully examined, they are found to differ from each other only by slight modifications, so that, in the majority of cases, the crystalline forms of each single substance can be grouped together under one *crystallographic system*, as it is called.

74. Numerous as crystalline forms are, they may all be included under six systems. Each of these contains a number of related, but dissimilar shapes, which agree in containing the same crystalline axes, as they are called. These axes are straight lines or directions within the crystal, passing through the same point, and terminating in the surfaces or angles of the crystal. Thus the first system is called the *octahedral*, or *regular* system of crystallisation. The three axes are at right angles to each other, and equal in length. The cube or hexahedron, which is one of the forms of this system, consists of six planes or squares, so arranged, that each is perpendicular to one axis, and parallel to the other two. The axes in this form terminate in the centre of each of the six faces of the crystal, as the figure will shew (see fig. 5, A).

75. In the octahedron, on the other hand, the axes terminate in the angles of the crystals, as the figure illustrates (see fig. 5, B). The connection between the cube and the octahedron may be well shewn by cutting a cube out of cork or soap, and paring away by degrees its corners, where four sides meet in a point. When this has been done sufficiently, an octahedron will be the result.

76. The other systems are named and characterised as follows: (2.) The *square prismatic* has the axes at right angles to each other, but two only of them equal in length, the third being longer or shorter than the other two. (3.) The *right prismatic* has the axes also at right angles, but all of different lengths. (4.) The *rhombohedral* has four axes, three of which are equal in length, in the same plane, and inclined to each other at angles of 60° ,

while the fourth is perpendicular to the others, and differs from them in length. (5.) The *oblique prismatic* has two of the axes intersecting each other obliquely, while the third is perpendicular to both, and unequal in length. (6.) The *doubly-oblique prismatic* has all three axes intersecting each other obliquely, and unequal.

77. The crystalline systems are best understood by connecting together wires, wooden rods, or pieces of stiff pasteboard, so as to represent the several axes, and then constructing around these some of the more common crystalline forms of each system. Rods of wood are most convenient, dovetailed into each other where they cross or intersect. Six of these will be requisite, if all the systems are to be illustrated, but fewer will suffice to make plain the scheme of crystalline systems.

78. By passing white cords or threads across the ends of the several rods, so as to connect them together, the resulting figure is seen to be one of the octahedrons of its system.

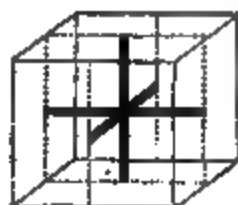
79. Square-faced, rectangular, or rhombic forms, such as the cube, the different prisms, and the rhombohedron, may be represented by means of wires.

80. The following figures represent two of the principal forms of five of the systems. The thick black lines correspond to the wooden rods or axes; the thin continuous lines are threads in the case of the octahedrons, and stout wires in the cube and prisms. The dotted lines in the figures of the latter are thin iron wires to receive and support the ends of the wooden rods. The same set of rods serves for two figures, A and B.

81. Without an extensive series of models, specimens, and drawings, the various crystalline secondary or derivative forms cannot be understood. Two models in each system of the chief figures would suffice to give a general conception of the differences in shape characteristic of each system. The following substances will afford specimens:

82. In the regular system, the majority of the metals represent the characteristic figures, also the diamond, fluor spar, iron pyrites, alum, galena, the garnet, &c.

Fig. 5. Regular System.—A, skeleton cube. B, skeleton regular octahedron; all the faces being equilateral triangles.



A



B

Fig. 5.

Fig. 6. Square Prismatic System.—A, a square prism. B, an octahedron with a square base; all the faces isosceles triangles.



A



B

Fig. 6.

Fig. 7. Right Prismatic System.—A, right prism. B, an octahedron with a rhombic base; all the faces scalene triangles.



A



B

Fig. 7.

Fig. 8. Rhombohedral System.—A, hexagonal prism. B, obtuse rhombohedron.



A



B

Fig. 8.

Fig. 9. Oblique Prismatic System.—A, oblique rhombic prism. B, octahedron of the same system.

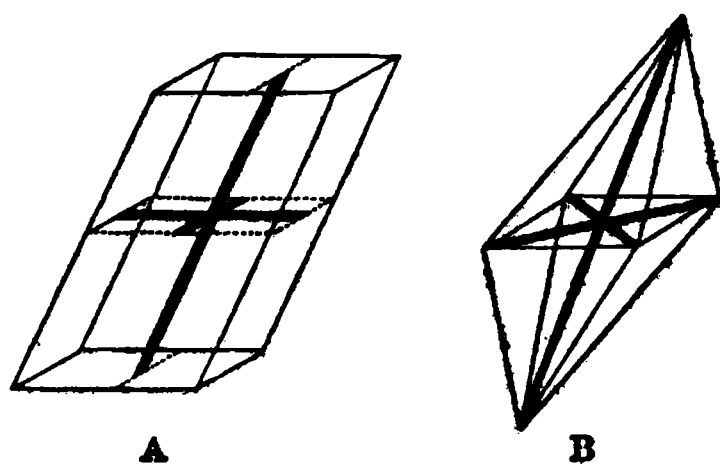


Fig. 9.

83. To the square prismatic system belong tinstone and potassic ferrocyanide. To the right prismatic system—potassic sulphate, sulphur, iodine. To the oblique prismatic—sodic carbonate and phosphate, borax, green vitriol. To the doubly-oblique prismatic system—cupric sulphate. To the rhombohedral system—calcareous spar, quartz, ice, arsenic, antimony.

84. Some bodies present an exception to the otherwise general law, that the crystals of one substance belong all to a single crystallographic system. Thus carbon, as the diamond, is a regular octahedron, and a member, therefore, of the regular system; as graphite or plumbago, it is a six-sided prism, which belongs to the rhombohedral system.

85. Sulphur, in like manner, crystallises when melted, in a shape belonging to the *oblique* prismatic system; when dissolved, in a shape belonging to the *right* prismatic system.

86. Sulphur, carbon, and the other bodies which present this character, are said to be *dimorphous*, from two Greek words signifying *two-shaped*.

87. On the other hand, certain substances which have decided chemical resemblances, are capable of replacing one another in a compound, without causing any alteration in its crystalline form. Thus, the two salts magnesian sulphate (Epsom salts) and zinc sulphate (white vitriol) are similar in constitution, except that the one contains magnesium in place of zinc. They both crystallise in the same form, a rhombic prism belonging to the right prismatic system, and cannot be distinguished from each other by the eye. So also the class of salts called alums all

crystallise in the form of a regular octahedron. Ordinary alum contains potassium and aluminium associated with sulphur and oxygen ; the potassium may be replaced by sodium, ammonium, silver, or thallium, and the aluminium by iron or chromium, and yet the resulting salt crystallises in octahedra.

88. Bodies which present this character are said to be *isomorphous*, a term signifying that they are possessed of the same shape. When substances are isomorphous, they frequently closely resemble each other in chemical properties.

CHAPTER V.

HEAT.

89. It has already been mentioned that heat is a powerful agent of decomposition in the chemist's hands, and several instances of its chemical effects have been given. In the present chapter, heat will be considered very briefly from a physical point of view.

90. The most important natural source of heat to us is the sun. The amount of heat received by the earth from the sun in a year would be sufficient to melt a stratum of ice 32 metres in thickness, and covering its entire surface.

91. Our artificial supplies of heat are almost wholly derived from chemical action. It will be seen in Chapter VIII., that heat is a general result of chemical combination, and all processes of burning consist essentially in the union of two or more substances, of the constituents of coal, for instance, with the oxygen of the air.* The construction of the different forms of apparatus for evolving and applying the heat of combustion, such as furnaces, blow-pipes, and gas-burners, will be more appropriately given in a later chapter.

92. Various theories have been held as to the nature of heat. It assuredly is not matter, according to our ordinary conception of matter. It is imponderable: a body when hot has absolutely

* Yet even here, it may be remarked, the sun is the ultimate source of the heat. Its rays caused the growth of the plants from which all our beds of coal are derived; and in our fires, we may be said to be enjoying the sun's heat which fell upon the earth in the ages when the carboniferous strata were being formed.

the same weight as the same body when cold. Heat is looked upon, therefore, as an affection of matter ; and modern research has rendered it most probable that it is a mode of motion, a vibration running through the molecules of a body, while the body, as a whole, is motionless. A greater intensity of heat will then correspond to a greater extent of vibration in the molecules, just as the loudness of a sound in air depends on the amplitude of vibration of the particles of the air.

93. This view of the nature of heat is much strengthened by the fact that we can convert visible motion into heat. Whenever motion is arrested or disappears, heat appears. A bullet, after being flattened against a target, often shews signs of melting ; and when brakes are applied to the wheels of a train, sufficient heat is often developed to set fire to the wood of the brake. Conversely, heat may be converted into motion. Thus, if we take a tube closed at one end and fitted with a movable piston, and if, when the piston is at the middle of the tube, we heat the closed end, the air below the piston will expand, and will cause it to move until it reaches the top of the tube. Now, if we measure accurately the temperature of the air, (1) at the moment the piston begins to move, (2) at the moment it reaches the top of the tube, we should find that some heat had disappeared in the latter case, corresponding to the amount of motion communicated to the piston.

EXPANSION.

94. The greater number of bodies, whether solid, liquid, or gaseous, which are not decomposed by heat, are expanded by it : in other words, occupy a greater space when hot than when cold.

95. Solids expand least, gases most, and liquids (speaking generally) are intermediate between them in expansibility.

96. To illustrate the expansion of solids, a rod of iron may be taken, and its length and diameter exactly measured at the temperature of the air. If it be now raised to a red heat, it

will be found to have suffered an increase in length, and to be too wide to fit an aperture through which it passed before. When allowed to cool to its original temperature, it will exactly recover its previous dimensions.

97. The expansion of liquids is familiarly illustrated by heating a glass flask filled with any liquid. The liquid rapidly expands, and manifests its expansion by running over.

98. Or a long glass tube, with a bulb at one end of it, may have the bulb filled with spirits of wine, or mercury, and then be plunged into hot water. The liquid will indicate its expansion by rapidly rising in the tube or stem of the ball. If it be now removed from the hot water, the enclosed liquid, as it cools, will descend till it reaches the point which it occupied at first.

99. The expansion of gases is most simply illustrated by introducing into a bladder, or other air-tight bag, a quantity of air, less than sufficient to fill it completely. If the bladder be now tied tightly round the mouth, and warmed at a fire, it will become fully distended by the expansion of the enclosed air. When withdrawn from the source of heat, the air will contract, and the bladder collapse again.

100. The expansion of gases may also be illustrated by inverting a flask with a long neck in water—the water being left standing to some height in the neck of the vessel. If a hot coal or heated plate of metal be now approached to the flask, the liquid will rapidly descend, forced before it by the expanding air. When the heat is withdrawn, the water rises to its previous height.

101. Nearly every solid and liquid has an expansibility peculiar to itself. Among solids, the metals are the most expansible bodies. Zinc expands most, platinum probably least, among bodies of the metallic class. Glass, brick, porcelain, marble, and stone have small expansibilities.

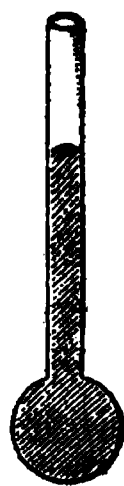


Fig. 10.

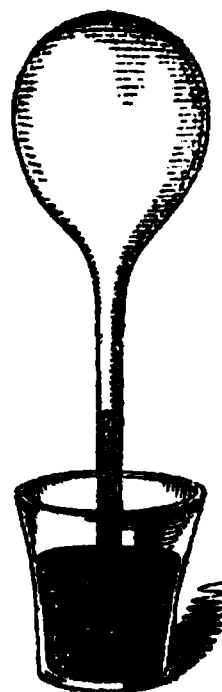


Fig. 11.

102. Among liquids, we find those which are most volatile more expansible than others. Thus, spirit of wine is six times more expansible by heat than mercury. The liquefied gases, the most volatile of known bodies, are more expansible in some cases than even air.

103. Water near its freezing-point presents a remarkable exception to the law that liquids expand by heat. If we gradually apply heat to ice-cold water, and examine its change in volume, we find that it contracts at first, and continues to do so until a thermometer (par. 118) placed in it marks 4° C. Beyond this point it expands, although far from regularly. It is for this reason that the temperature 4° C. is mentioned in defining the gramme (par. 54), since at this point a certain weight of water occupies the smallest volume that it can ever occupy, under ordinary pressures. This peculiarity of water has a very great influence in modifying natural phenomena. Since heavier fluids sink through lighter fluids, if water contracted in volume regularly down to its freezing-point, the coldest water in a lake or river would be at the bottom, and ice would first be formed there, receiving continual additions as the cold surface-water descended; and thus, in a severe winter, our lakes and rivers would become solid masses of ice, and all fish in them would perish. As soon as the whole mass of water has cooled to 4° C., the surface water ceases to descend, although gradually cooled down to the freezing-point; and, since it undergoes a further expansion at the moment of becoming ice, the latter swims on the surface, and the main body of the water never falls below the temperature of 4° C.

104. Gases, unlike solids and liquids, have not specific expansibilities, but each undergoes the same amount of expansion for the addition of the same amount of heat; or, at all events, the departure from exact identity in expansibility is so slight, that it may be disregarded in all but very delicate researches. Thus, if we were to take common air, hydrogen, and carbonic dioxide, and heat them equally, we should find that they all suffered the same amount of expansion; whereas, if we took any three solids or liquids, and heated

them equally, we should find that each expanded to a different extent.

105. The law expressing the amount of dilatation of gases by heat may be thus stated: For every increase in temperature of 1° centigrade, a gas expands $\frac{1}{273}$ ($=0.00366$) of the volume it occupies at 0° centigrade. Thus, if we take 1 litre of any gas at the temperature of the freezing-point of water, and heat it 1° centigrade, keeping the pressure upon it constant, it will become 1.00366 of a litre; if we heat it to 100° centigrade, it will become 1.366 of a litre; and so on.

106. From this fact it is easy to calculate the change in volume a gas would undergo when heated from any temperature to any other temperature. For instance, supposing 200 c.c. of a gas were measured at 15° C., and we wished to know what volume the gas would occupy at 120° C., the problem might be solved in the following way. We know that 1 litre of a gas at 0° C. becomes $(1 + .00366 \times 15 =)$ 1.0549 of a litre at 15° C., and $\{1 + (.00366 \times 120) = \}$ 1.4392 of a litre at 120° C.; and the expansion of our 200 c.c. of gas must be in the same proportion. Hence, $1.0549 : 1.4392 :: 200 : 272.8$ —that is, the 200 c.c. would measure 272.8 c.c. at 120° C.*

107. Solids and liquids expand more at high than at low temperatures; that is to say, an amount of heat which would expand them to a certain extent, if they, at the period of its application, were at the temperature of the air, would expand them to a greater extent if, at the moment of its reception, they were at a higher temperature, such as a red heat. This has also been observed to be the case with gases, though not to so great an extent; and it may be stated generally that the

* In calculating vapour-densities (par. 63), it is necessary to ascertain the weight of a given volume of a gas at a certain temperature. If we know the weight of 1 c.c. of it at 0° , the method of performing the calculation will be evident from what is said above. Thus, supposing it were required to ascertain the weight of 200 c.c. of air at 120° C. According to the law, 1 c.c. of air at 0° would become $\{1 + (.00366 \times 120) = \}$ 1.4392 c.c. at 120° . And, since 1.4392 c.c. of air at 120° would contract to 1 c.c. at 0° , therefore 200 c.c. at 120° would become 138.9 c.c. at 0° . Now, the weight of 1 c.c. of air at 0° is 0.001293 grm. Hence 138.9 c.c. will weigh $(0.001293 \times 138.9 =)$ 0.1798 grm. The height of the barometer is assumed to be 760 mm.

nearer a substance is to the temperature at which it changes its state, the more irregular its expansion becomes.

THE THERMOMETER.

108. The thermometer is an instrument in which *temperature*—that is, the *intensity of heat*—is measured by the amount of expansion it produces on solids, liquids, or gases. Solids expand too little, gases too much, to be practically available for the construction of thermometers. The only one, accordingly, to which we shall refer is the liquid thermometer universally in use.

109. The liquids employed to measure heat are two—namely, spirits of wine, or alcohol, and quicksilver. The former is employed for instruments intended to measure low temperatures, for which purpose quicksilver is inapplicable, as it freezes, or becomes solid, if too much heat be withdrawn from it; whereas the strongest spirits of wine cannot be congealed by any known cold. For ordinary temperatures, however, mercury is preferable to alcohol.

110. That the expansions and contractions of the mercury or spirits of wine may be visible, the liquid is enclosed in a vessel of transparent glass. This consists of a glass tube, with a very fine bore, at one extremity of which a spherical or cylindrical bulb is blown. The liquid is introduced by heating the bulb until some of the air it contains has been driven out by expansion. The open end of the tube is then quickly dipped into the liquid, and some of the latter is forced in, as the bulb cools, by the pressure of the external air. The liquid in the bulb is next boiled for a short time, that the vapour may chase out the remaining air, and the open end is again dipped into the liquid, which, when the vapour is condensed, rises and fills the bulb entirely. The quantity of liquid introduced is so adjusted as to fill the bulb and a small portion of the tube at the lowest temperature which the thermometer is intended to indicate. The bulb is then heated until the column of liquid

fills the whole of the tube, and the open end is closed, or hermetically sealed, by melting it in a blow-pipe flame.

111. The instrument, as thus constructed, would only tell that one body was hotter or colder than another, without shewing by how much the one exceeded or fell short of the other in temperature. Before it can record this, it requires to be what is called *graduated*; in other words, to have points marked on it which correspond to certain invariable temperatures or intensities of heat.

112. If ice or snow be placed in water, and allowed to melt there, whilst a thermometer is plunged into the water, the mercury or spirit of wine within the instrument will be found to stand immovably at a certain height. This phenomenon is more briefly described by saying that *the thermometer* stands at a certain height; the reference in this and similar expressions being to the enclosed liquid and its risings and fallings, which measure the variations in the intensity of the heat. If we leave the thermometer in the melting ice, it will stand steadily at the same point as long as any of the ice or snow is unmelted. However often we repeat this experiment, the thermometer will always stand at the same height, because melting ice always exhibits the same intensity of heat, or, as it is called, the same temperature.

113. In graduating a thermometer, accordingly, it is first plunged into melting ice, and left there till the enclosed liquid stands still. A mark is then placed on the glass, or on a piece of ivory, wood, or metal attached to the tube, and called its *scale*. This mark or horizontal line is drawn exactly on a level with the surface of the enclosed mercury or spirits of wine whilst the instrument is still in the melting ice; and this mark is called the *freezing-point* of water, for water freezing and ice melting produce the same temperature.

114. The thermometer is now transferred to a vessel containing water kept at its boiling-point, the experiment being made when the barometer stands at 760 mm. The instrument rapidly rises as it acquires heat from the water, but finally ceases to ascend, and remains steadily at the same point,

however long it is kept in the boiling water. A second mark is placed at the surface of the liquid within the thermometer tube, and this is called the *boiling-point*.

115. On the system introduced by Fahrenheit, which is not yet superseded in this country, the space upon the stem or scale of the instrument between the

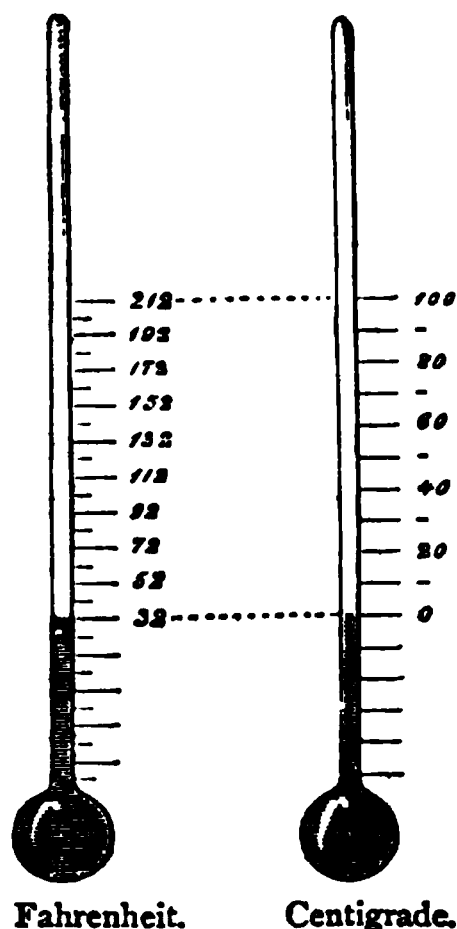


Fig. 12.

freezing and boiling points is divided into a hundred and eighty equal parts, which are called degrees, and indicated by a small circle, thus $^{\circ}$. Divisions or degrees of the same value are then extended above and below the freezing and boiling points to a distance from each, varying according as the instrument contains mercury or spirits of wine, and is to be used for estimating high or low temperatures. A mercurial thermometer cannot be graduated lower than 39° below zero, or 0° on Fahrenheit's scale, at which temperature mercury congeals. It may be graduated upwards to 570° above the freezing-point, but not higher.

116. There is no limit to the downward graduation of a spirit-thermometer, as the greatest attainable cold does not freeze its liquid. It boils, however, at 141° above the freezing-point, so that its upward graduation is much more limited than that of the mercurial thermometer.

117. The scale in Fahrenheit's thermometer begins at 32° below the freezing-point. A cipher is placed there, and it is called the zero, or starting-point of the thermometer. The freezing-point of water thus comes to be marked by the number 32° , and the boiling-point, which is 180° higher, by 212° . Thus we say that a mixture of salt and snow reduces the thermometer to 0° , that the freezing-point of water is 32° , and that its boiling-point is 212° .

118. On the centigrade system of graduation, the space between the freezing and boiling points of water is divided into 100 equal parts, and the graduation begins at the freezing-point, which is marked 0° , or zero. According to this thermometer, water freezes at 0° , and boils at 100° .

119. The centigrade thermometer is now almost always employed in scientific researches in this country, and will be the only one employed in this book. To prevent any confusion arising from its being mistaken for the thermometer first described, which is called, from its original maker (who was a Dutchman), Fahrenheit's, or the Fahrenheit thermometer, the letter F. is placed after temperatures indicated by his thermometer, and the letter C. after those denoted by the centigrade. Thus, water freezes at 32° F., or 0° C.; water boils at 212° F., or 100° C.

120. From its zero point each thermometer counts downwards as well as upwards; and to distinguish the degrees below zero from those above it, the former are distinguished by prefixing to them the minus sign $-$. Thus mercury is said to freeze at -39° F.; that is, at 39° below zero, or 0° on Fahrenheit's scale.

121. It is often necessary to convert temperatures expressed on the Fahrenheit scale into the corresponding temperatures on the centigrade scale. This will be easy, if it is borne in mind that the same space (that is, that through which the liquid moves between the freezing and the boiling point of water) is divided on the Fahrenheit scale into 180° , on the centigrade scale into 100° . Hence, 180° Fahrenheit are equal to 100° centigrade; that is, 1° F. to $(\frac{100}{180} =) \frac{5}{9}^{\circ}$ C.; and 1° C. to $(\frac{180}{100} =) \frac{9}{5}^{\circ}$ F. We must, then, multiply Fahrenheit degrees by $\frac{5}{9}$ to reduce them to centigrade, and centigrade degrees by $\frac{9}{5}$ to reduce them to Fahrenheit. This would be all that is necessary if the two scales started from the same point. But on the centigrade scale the zero is at the freezing-point of water, while, on the Fahrenheit scale, it is 32° below. Hence, we must add or subtract 32, as the case requires, in order to

bring the scales to the same starting-point. The rule then will be :

(1.) To convert Fahrenheit degrees into centigrade degrees : Subtract 32 from the number of degrees, and multiply the remainder by $\frac{5}{9}$ (or 0.5).

(2.) To convert centigrade degrees into Fahrenheit degrees : Multiply the number of degrees by $\frac{9}{5}$ (or 1.8), and add 32 to the product.*

122. It is of the utmost importance for the student to understand what information concerning heat the thermometer supplies. In a word, then, it tells us nothing as to the *quantity* of heat in a body ; in proof of which we have only to try the simple experiment of plunging the same thermometer into a large basin of water, and then into any smaller quantity, such as a wine-glassful, taken out of the basin. The thermometer will stand at the same height in both, although it is manifest that there must be much more heat in the basinful than in the wine-glassful of water.

123. What the thermometer reveals to us is the *intensity* of the heat which affects it, as measured by its power to cause expansion. This intensity we distinguish by calling it *temperature*. Thus, if we say that a body has the temperature of 60°, we signify that it expands the mercury or spirit in the thermometer to the 60th degree.

124. When directions are given, as they constantly are, to raise the temperature of a body (from 60°, for example) to 300°, they signify that heat is to be added to the substance till it is present in a state of intensity sufficient to raise the thermometer to the 300th degree. It is often of the utmost importance in the drying, for example, of such bodies as gunpowder, or gun-cotton, to raise them to a certain temperature without exceeding this by a single degree. The thermometer enables this to be done with the utmost precision.

* To take an example : Alcohol boils at 173° F., what is this on the centigrade scale ? $173 - 32 = 141$, and $141 \times \frac{5}{9} = 78.3$ ° C.

Again, mercury freezes at - 39.4° C., what is this on the Fahrenheit scale ? $- 39.4 \times \frac{9}{5} = - 70.9$, and $- 70.9 + 32 = - 38.9$ ° F.

125. To sum up what we have said in a word. The thermometer is a measurer of the intensity of heat, but not of its quantity, unless we are dealing with the same substance. It is found that, within a moderate range of temperature, the amount of heat required to raise a given weight of water 2° , 3° , &c., is twice, three times, &c., as much as that required to raise it 1° .

126. It is convenient, in dealing with many problems relating to heat, to assume some unit of heat, just as we agree upon some unit of measure and weight; and the quantity of heat which is universally accepted as the unit is THE AMOUNT OF HEAT REQUIRED TO RAISE 1 KILOGRAMME OF WATER FROM 0° TO 1° C.

SPECIFIC HEAT.

127. Different substances require different quantities of heat to raise them to the same temperature. This is expressed by saying that each possesses a *specific capacity* for heat, or, more shortly, a *specific heat*.

128. The fact can easily be proved in three different ways. 1st, We may expose a variety of substances to the same source of heat, when we shall find that some of them rise more rapidly in temperature than others; and if, after they have all risen to the same temperature, they are removed to a cold apartment, those which grew hot fastest will be found also to cool most quickly, because a smaller amount of heat has sufficed to raise their temperature than that of the others, and they have the less to part with when they cool. Thus, if two vessels, containing, the one mercury, the other water, in equal measures, and at the same temperature, be immersed in a vessel containing water in a state of ebullition, the mercury will be found to rise to the temperature of the boiling water in half the time that the water does. If both, after having reached the same temperature, be set aside to cool, the mercury will fall in temperature twice as fast as the water does.

129. 2d, If we cause equal weights of bodies, which have all been raised to the same temperature, to melt ice, we shall find

that a much greater weight of it will be melted by one body than by another. Thus, mercury at 100° will melt much less ice than an equal quantity of water at the same temperature will, for the mercury has much less heat to give out, so as to produce liquefaction, than the water has.

130. 3d, If we mingle two portions of liquid, at different temperatures, the temperatures of the resulting mixture will vary according to the liquids taken. If, for example, we mingle equal weights of water, the one at the temperature of 100° , and the other at 0° , the resulting mixture will have the temperature 50° , the arithmetical mean of 100 and 0; or the hot water will lose 50° of heat, and the cold will gain exactly as many.

131. In like manner, if we mix mercury with mercury, or oil with oil, the temperature of the mixture will be the mean of the temperatures possessed by the different portions of the liquid which were mingled. If, however, one liquid at a certain temperature be added to a different liquid at a different temperature, we shall not get the arithmetical mean, but something above or below it. Thus, if we add a kilogramme of mercury at 100° to a kilogramme of water at 0° , the temperature of the mixture is 3.2° , instead of the mean 50° . The mercury has become less warm by 96.8° , whilst the water has grown warmer by 3.2° only; yet the heat which the water has gained is the very same quantity which the mercury has lost.

132. If, on the other hand, we take a kilogramme of water at 100° , and mix it with a kilogramme of mercury at 0° , the resulting temperature is 96.8° , or the water becomes less warm by 3.2° , and the mercury grows hotter by 96.8° . It thus appears that the same amount of heat exhibits a higher intensity when contained in quicksilver than when contained in water.

133. In the preceding illustrations we have referred only to liquids, but exactly similar experiments can be made with solids, and to a certain extent with gases. The last, however, present many difficulties in experimenting upon them, so that there is some uncertainty concerning their specific heats.

134. Solids are easily experimented on, and most simply, by

raising them to a certain temperature, and plunging them into water or another liquid at a lower temperature. This is equivalent to the mixture of one liquid with another.

135. Specific heats are generally stated with reference to equal weights, rather than to equal measures, of bodies. Thus, in the above example, the water lost 3.2 units of heat (par. 126), and this quantity of heat has raised an equal weight of mercury 96.8° . Hence, 1 unit of heat would raise a kilogramme of mercury ($\frac{96.8}{3.2} =$) 30.25° ; and if we define the specific heat of a substance to be the number expressing the quantity of heat required to raise 1 kilogramme of it from 0° to 1° in temperature, we shall obtain ($\frac{1}{30.25} =$) .033 as the specific heat of mercury; the specific heat of water being 1.000. The following table has been constructed on this principle.

| Substances. | Specific Heat of Equal Weights. |
|--------------------|---------------------------------|
| Water..... | 1.000 |
| Ice..... | .513 |
| Wood Charcoal..... | .241 |
| Sulphur..... | .203 |
| Glass..... | .198 |
| Diamond..... | .147 |
| Iron..... | .1138 |
| Copper..... | .09515 |
| Silver..... | .05701 |
| Iodine..... | .05412 |
| Gold..... | .03244 |
| Mercury..... | .0333 |

136. The great specific heat of water has a most important relation to the welfare of the living creatures on the globe. The sea, which spreads over so large a portion of the earth, cannot in the hot seasons of the year become rapidly raised in temperature, which would prove injurious alike to its inhabitants and to the dwellers on the dry land. Rapid elevation of temperature cannot occur, in consequence of the great amount of heat which must be absorbed by water before it can manifest even a moderate increase in warmth.

137. In the cold seasons of the year, on the other hand, the

sea and other great beds of water cool slowly, and, moreover, in cooling, evolve much heat, which equalises the temperature of the air as well as that of the land. An ocean of mercury, even if otherwise habitable by the creatures with which we are familiar, would suffer so great an alteration in temperature during the twenty-four hours of a tropical day and night, as to prove fatal to multitudes, if not to all of them.

138. The small specific heat of mercury is nevertheless most advantageous to the chemist. It renders that liquid the fittest of all for filling thermometers, as it quickly heats, and quickly cools, and acquires, in consequence, with great rapidity, the temperature of any body in which the thermometer is placed.

139. No relation can be perceived between the numbers expressing the specific heats of different substances, as given in the preceding table. If, however, instead of taking *equal* weights of bodies, as is done in that list, we take quantities proportional to their atomic weights, then a very simple and beautiful relation is found to subsist between the specific heats of different bodies.

140. Thus, instead of trying how much the temperature of water at 0° will be raised by plunging into it a kilogramme of sulphur, a kilogramme of iron, and a kilogramme of phosphorus, each at 100° , let us take 32 kilogrammes of sulphur, 56 kilogrammes of iron, and 31 kilogrammes of phosphorus, or any other quantities, so that they be in the ratio of 32, 56, and 31—the atomic weights of sulphur, iron, and phosphorus. Let these equivalent quantities be then raised to the same temperature, 100° , and afterwards immersed in water at 0° , so as to observe how much each raises the temperature of the liquid. On making such an experiment, we shall find that the 32 parts of sulphur, and the 56 of iron, and the 31 of phosphorus, will raise the water to exactly the same temperature. It thus appears that the capacity for heat of these substances, when taken in quantities proportional to their atomic weights, is identical.

141. The same is true of nearly all the elements with which

the chemist is acquainted, and the general law, discovered by MM. Dulong and Petit, may be thus expressed: THE PRODUCT OF THE SPECIFIC HEAT OF AN ELEMENT, MULTIPLIED BY ITS ATOMIC WEIGHT, IS A CONSTANT QUANTITY = 6.4 or nearly so.

142. Thus, in the case of the three elements above mentioned, we have :

| | Specific Heat. | Atomic Weight. | Product. |
|--------------------------|----------------|----------------|----------|
| Sulphur..... | .2026 | 32 | 6.48 |
| Iron..... | .1138 | 56 | 6.37 |
| Phosphorus (liquid)..... | .212 | 31 | 6.57 |

Carbon, boron, and silicon form remarkable exceptions to this law, the product of the specific heat into the atomic weight being, in the case of carbon (diamond), 1.76; of boron, 2.75; of silicon, 4.97.

143. Compound bodies have also been found to exhibit an identity or simplicity of relation, so far as specific heat is concerned; but this department of the subject cannot be enlarged on here.

144. The above facts afford a good illustration of the value to the chemist of physical data. The determination of the specific heat of a body is considered of great importance in fixing the weight of its atom; and it has mainly led to the recent change of the atomic weights of a large group of metals such as zinc and iron.

PROPAGATION OF HEAT.

145. Heat is transferred from one portion of matter to another in three different ways, which are termed conduction, convection, and radiation.

146. CONDUCTION implies the passage of heat from one particle of matter to another in physical contact with it.

147. CONVECTION is the conveying or carrying of heat by particles of matter raised in temperature, and set in motion.

148. RADIATION is the emission of heat by a body such, for example, as a mass of red-hot iron at rest, and not in physical contact with the substances to which it communicates

heat. The name has reference to the supposition that the heat passes in radii or rays like those of sunlight, which can find their way even through the best vacuum we are able to produce.

Conduction.

149. Conduction is best seen in solids, and particularly in metals, which are the best conductors. A rod of iron placed with one extremity in the fire speedily becomes hot at the opposite extremity, owing to the conduction of heat from particle to particle along the rod. But metals differ considerably in their power of conducting. If a rod of iron and a rod of copper of equal size and length be joined end to end, and heated at their point of junction, a piece of phosphorus placed on the further extremity of the copper will take fire much sooner than a piece placed in a similar position on the iron. Since these two metals do not differ much in specific heat, the result must be due to the greater rapidity with which heat travels through the copper.

150. Dense bodies are generally the best conductors; light and porous ones the worst. Feathers, down, fur, flannel, and most of the fabrics used for winter dresses, owe their so-called warmth to their low conducting power for heat. Their action is altogether negative, being limited to the prevention of the rapid escape of heat generated by the living beings whose bodies they cover.

151. Liquids and gases are very bad conductors of heat, although, from the rapidity with which they rise in temperature, when heat is applied to them, they would appear to be among the best conductors.

Convection.

152. Liquids and gases rise in temperature chiefly in consequence of the convection, not the conduction of heat by their particles. If a long glass tube shut at its lower end, and filled nearly to the top with water or any other liquid, be placed obliquely, and a spirit-lamp applied so as to heat the upper

portion of the tube and of the liquid, the latter will rise in temperature at the point heated, and above that, till ebullition occurs. Below the point to which the lamp was applied, the temperature of the liquid will be very slightly elevated, and hours will elapse before the heat will have sensibly affected, even to a very slight degree, the column of liquid below it. Now, the conduction of heat is not affected by the position of the body along which it is passing. Heat descends as readily as it ascends, and moves as swiftly along a body placed vertically as horizontally. Had the heat then been conducted, it would have travelled down the column of liquid as readily as up through it.

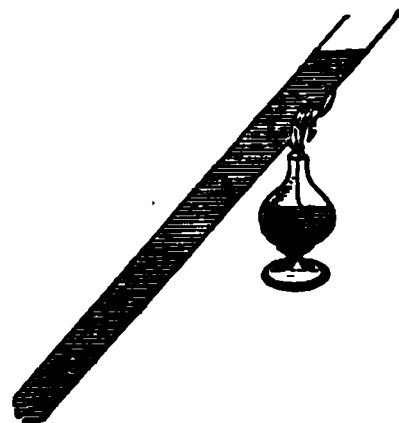


Fig. 13.

153. On the other hand, no fact is more familiar than that large quantities of liquid may be made to boil by even a small lamp, provided only the heat be applied at the bottom. Thus, if we transfer the lamp from near the top of the long tube to the shut lower end of it, the whole liquid in the tube will be made to boil in a few minutes.

154. The remarkable difference observed in the latter case as to the rapidity of transference of heat, is easily explained. If a pretty large glass flask be taken (fig. 14), and a few fragments of solid blue *litmus** dropped into it, after it has been filled nearly full of water, on applying heat by a small lamp to the bottom of the vessel, a central current of water, rendered distinctly visible by the blue colour it has acquired from the litmus, is seen to ascend till it reaches the surface of the liquid, when it bends over in every direction like the foliage of a palm-tree, and forms a number of descending currents. These keeping pretty near to the walls of the vessel, travel downwards till they reach the heated lower portion of it, when they again ascend as a hot central current. In this way the whole liquid is thrown

* A colouring matter prepared from certain lichens, and readily procured from any druggist or dealer in dye-stuffs.

into circulation, for every portion of it in turn becomes heated, ascends, and losing its heat in and after its ascent, chiefly by parting with it to the walls of the vessel, the air, and surrounding objects, descends as a cold current till it reaches the bottom, when it becomes heated again.

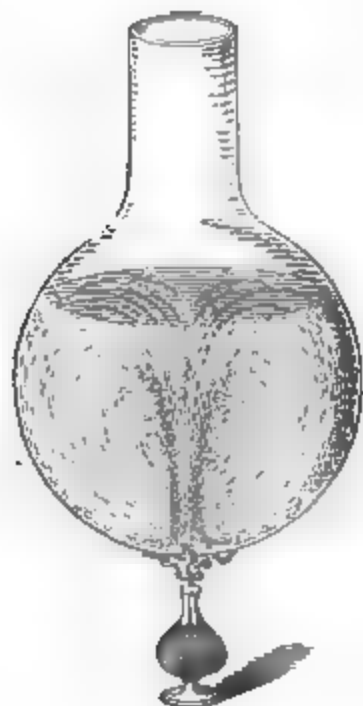


Fig. 14.

155. The currents which are thus occasioned by heating a liquid are determined by the fact, that when any portion of liquid is warmed, it expands, and has, in consequence, its specific gravity lessened. In other words, a portion of warm liquid is less dense than an equal volume of cold liquid. The result of this is, that the heated portions of the liquid being specifically lighter than the colder ones, ascend through the latter, till they reach a

part or region of the liquid of the same density as themselves, and thus there is a constant ascent of lighter warm liquid, and descent of colder heavy liquid, so long as heat is applied.

156. A liquid is thus raised in temperature mainly by the operation of two causes. The one is the movement of particles through the liquid carrying heat with them, and giving this up in part to the colder molecules which they meet. This is what is styled the convection—that is, the conveyance or carrying of heat.

157. The other chief cause of the rapid rise of a liquid to its boiling-point, when heated from below, is the fact, that the circulation which convection determines, brings every particle of liquid in its turn to the source of heat, which directly effects the elevation of its temperature. Thus, whilst a solid is heated by the particles remaining at rest, and the heat travelling from one to another, a liquid is warmed by the heat confining itself almost entirely to one spot, whilst the particles of the liquid

travel towards that, and receive and carry away with them certain quantities of heat. It must not be forgotten, however, that a certain amount of heat is propagated in all directions through liquids by conduction.

158. A double siphon, as represented in fig. 15, containing coloured water in the lower part, with the rest of the arrangement filled with colourless liquid, illustrates the circulation of heated liquids very beautifully. A lamp is to be applied at either of the lower corners, as shewn in the figure, when the coloured liquid will be seen to rise from it, and ascend the heated limb of the rectangular tube. Simultaneously the colourless water will descend in the opposite limb, and the whole contents of the arrangement will be thrown into motion, and continue to circulate so long as the heat is applied. An apparatus upon this principle is now employed to heat apartments.



Fig. 15.

159. Gases are raised in temperature in exactly the same way that liquids are. They conduct heat extremely slowly, which may be proved by enclosing any one of the gases in a glass jar, containing a delicate thermometer with its bulb placed nearly on a line with the mouth of the jar. If the vessel be now shut by an air-tight metallic cover, and sulphuric ether or any other combustible be burned upon the lid so as to raise its temperature, it will be found that this may be done for a long period without the thermometer rising, although it is placed only a little below the heated metal. After a time, however, the metal begins to radiate heat from its lower surface, and this raises the thermometer.

160. If heat, on the other hand, be applied from below to a gas contained in a vessel, the former becomes, like a liquid in the same circumstances, warmer, and specifically lighter, and ascending and descending currents rapidly effect the elevation

in temperature of the whole mass of gas. Illustrations of this are familiar to every one. The column of smoke which rises from a fire is merely a current of heated air rendered visible by the soot which it carries with it. Its place is supplied by descending currents of heavier cold air, which in their turn are heated, and become light ascending ones. The roaring noise which is heard at the mouth of a furnace-door or stove is occasioned by the streams of cold air which rush in to supply the place of the column of heated gases constantly rising through the chimney.

161. It is a popular belief that a large fire in the open air makes the wind rise; and so far it is quite true. The fire can only be maintained by constant lateral and descending streams of cold air to supply the place of the ascending column. When Moscow was burned, the wind rose so high, that men and horses could with difficulty keep their feet whilst passing through the burning streets.

162. On the small scale, the circulation which occurs in heated gases may be shewn by burning any substance, such as brown paper or tow, which gives a smoky flame, under a glass bell-jar. A small portion of combustible only should be taken and placed on a pedestal within the glass shade or bell-jar. A much better method, however, is to kindle a piece of roll sulphur, placed in a small cup raised upon a stalk, and then to cover it with a glass shade or globe filled with oxygen. The sulphur, in burning, produces white fumes (sulphurous acid mingled with water vapour), which rise vertically from the combustible, and ascend till they strike the dome of the bell-jar or globe, when they bend over in every direction, and travel downwards to the bottom.

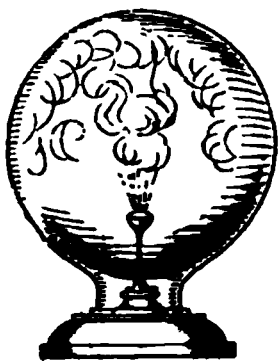


Fig. 16.

Radiation.

163. Radiation, though one of the most important modes in which heat travels from one body to another, does not very

particularly concern the chemist. The following points with regard to it are all we need mention : Every hot body in the act of cooling, besides losing heat by the conductive and convective action of the solids and fluids in its neighbourhood, parts with much heat by radiation. Rays of heat pass away from the hot body till it has reached the temperature of the air or surrounding medium. In proof of this, it is only necessary to hang a hot body in the vacuum of the air-pump, when it rapidly cools, although it does not lose heat by either conduction or convection.

164. Heat, when propagated by radiation, obeys the same laws as light : indeed, the two modes of vibration which we call heat and light are very closely connected, and appear to differ only in velocity. Thus, when a piece of iron is heated, it sends out at first rays of heat, which do not affect the eye ; as it becomes hotter, however, rays are emitted which produce on the eye the sensation of red. The body becomes, as we say, *red-hot*, and is emitting both heat- and light- rays.

165. The rate of cooling of a hot solid body, so far as radiation is concerned, is remarkably influenced by the state of its surface, and, in the case of liquids and gases, by the state of the surface of the vessels containing them. Thus, hot water placed in a tin vessel coated externally with lampblack, cools twice as fast as it does in a bright tin vessel. Similarly, if two metallic vessels be taken, the one left bright, and the other covered with linen, hot water will be found to cool much faster in the covered than in the naked vessel.

166. From these observations, it appears that a kettle covered with soot is much less suited for retaining water warm, than if it had a polished metallic surface. So, also, bright metallic covers are the best at table, and metallic tea-pots and coffee-pots are preferable to those of porcelain and stoneware.

167. If we inquire what kind of surface is the best absorbent of radiant heat, we find a very remarkable connection between radiation and absorption. The best radiators are, without exception, the best absorbers. Thus, if a red-hot ball is placed

exactly midway between two sheets of tin, the one of which is covered with lampblack, the other brightly polished, it is found that the blackened surface becomes hot much sooner than the polished one. Hence, water will boil much sooner in a kettle covered with soot than in one which is brightly polished, when neither are in immediate contact with the hot coals.

168. The heat of the sun, in radiating towards the earth, passes through the atmosphere without raising it in temperature, except to a very small extent. In consequence of this, the higher regions of the atmosphere, though nearer the sun, are much colder than the lower, which are raised in temperature by the transference to them of heat from the warm earth.

LATENT HEAT.

169. When a solid body, such as ice, is watched whilst melting, a large quantity of heat is observed to enter it without raising its temperature in the slightest degree.

170. This heat which enters the body serves only to melt or liquefy it, without rendering the liquid the least hotter than the solid was which yielded it. The water which flows from the melting ice is no warmer than the ice.

171. The heat which thus renders a body liquid without warming it, is called *latent* or *insensible* heat, because it does not affect our sensations, and does not raise the thermometer.

172. It is, as it were, so completely occupied in maintaining liquidity, that it is unable to exhibit its otherwise characteristic properties of exciting in our bodies the sensation of warmth, and of elevating the thermometer. In illustration of the truth of this, the following experiments may be tried.

173. If a piece of ice be hung up in a warm room, it will be found to melt very slowly, which would not be the case if the addition of a small quantity of heat to frozen water served to convert it into liquid water. And that the slowness of its melting is owing to the large quantity of heat which it is under the necessity of gathering from the bodies around it, and which is totally expended in liquefying it, may be proved by holding

the hand, or placing a thermometer, below the piece of melting ice, when a stream of cold air will be found constantly descending from it.

174. Another striking mode of proving the absorption and apparent disappearance of heat during liquefaction is the following: Let a kilogramme of ice be taken, and, in addition, a quantity of water equal to it in weight. The temperature of the water is then to be lowered to 0° , and the ice and water removed to a warm room, whilst a thermometer is placed in the water, so as to observe how many degrees it rises during a given portion of time, say half an hour. Let us suppose that the warmth of the room is such, that in this period the thermometer rises 4° , and that the temperature of the room is kept the same as it was at the beginning of the experiment, till the whole of the ice is melted. This will require some hours; and as the ice, like the water, has been gaining 8 units of heat each hour, we shall be able to ascertain both that heat disappears, and how much of it becomes latent, during the melting of the ice.

175. In a trial of this kind made by Dr Black, the discoverer of latent heat, ten hours and a half elapsed before the ice, originally at 0° , had melted. The temperature of the ice-water was then 4.4° above the freezing-point. During the period mentioned, the ice had been receiving heat at the rate previously mentioned (4° every half-hour), so that, if we multiply 4° by 21 (the number of half-hours), it will give us 84° , which should have been the temperature of the ice-water, if none of the heat which entered it had become latent. Its temperature, however, was only 4.4° , and it had risen to this point after it had undergone complete liquefaction. If we subtract 4.4 from 84 it will leave 79.6, the number of units of heat which had been absorbed by the melting ice without raising its temperature. In other words, before ice can become water, as much heat must be absorbed by it, and become latent, as would, if free, expand the thermometer through 79.6° . This result only slightly differs from that of the more modern determinations of Regnault.

176. The most decisive, however, of all ways of demonstrating the latency of heat, is to mix a certain quantity, say a kilogramme of ice, or, still better, from its state of division, of snow at 0° , with a kilogramme of water at 79° . The result will be found to be that the snow is all melted, and two kilogrammes of water are procured at the temperature of 0° . The hot water, in cooling from 79° to 0° , has lost 79° of heat, which changes the snow into water, but does not raise its temperature above that originally possessed by the snow.

177. The striking nature of the last experiment will be rendered more apparent if it be contrasted with the effect of mixing a kilogramme of *water* at 0° with a kilogramme at 79° . The temperature now, instead of being 0° , will be the mean of the two temperatures, or 39.5° .

178. What we have illustrated here with ice holds good for all solids. Each one of them renders latent a certain quantity of heat in becoming liquid, and retains that heat so long as it remains liquid. The following table shews the amount of heat which disappears during the liquefaction of several solids, and which is distinguished as their latent heat :

| | Latent Heat. |
|--------------|-----------------|
| Water..... | 79° |
| Sulphur..... | 9.4° |
| Lead..... | 5.4° |
| Tin..... | 14.25° |

179. Let us inquire what explanation of latent heat can be given on the theory that heat is molecular motion. The heat which seems to disappear during the conversion of a solid into a liquid, and a liquid into a gas, is really spent in doing mechanical work, in forcing the molecules farther from each other in opposition to the force of cohesion. The heat is not lost, any more than the mechanical force expended in raising a weight is lost; it can be entirely accounted for, and will reappear as heat when the gas is re-converted into a liquid, and the liquid into a solid.

180. The slowness with which water generally freezes, makes

it more difficult to demonstrate the evolution of heat during congelation than the disappearance of it during liquefaction. By the following experiment, however, in which a different substance than water is made to solidify, the fact may be proved very strikingly :

181. A flask full of water is to be placed over a lamp till the water boils. Sodic sulphate (Glauber's salt) is then to be added in small successive quantities, as long as the water will dissolve it, and when the boiling liquid is thus saturated, it is to be rapidly corked whilst the vapour is still issuing, and the light withdrawn. The flask is then to be set aside, and left perfectly undisturbed for several hours, so that it may slowly cool to the temperature of the air.

182. If such a solution as we have described were exposed in an open vessel, and especially if agitated, it would begin to deposit crystals soon after it was set aside, for boiling water dissolves a much greater amount of Glauber's salt than cold water can retain in solution ; and accordingly, as the temperature of the liquid falls, the sodic sulphate gradually separates, and adheres in crystals to the bottom and sides of the vessel. If the corked flask, however, be not disturbed, the solution may be cooled even to 15° without a single crystal separating. If, then, the cork be withdrawn, and the liquid shaken, or, still better, if any rough body be dropped in, the whole amount of sodic sulphate, which water at 15° cannot dissolve, suddenly becomes insoluble and solid, and the liquid appears in a moment to freeze or congeal so completely, that the flask may be turned upside down without a drop of fluid escaping. This sudden conversion of liquid sodic sulphate into solid sodic sulphate, is a phenomenon of exactly the same kind as the sudden freezing of water would be, and is accompanied by the evolution, in a sensible form, of all the heat which, whilst in a latent state, kept the salt liquid, or in solution. Accordingly, if the flask be grasped in the hand at the moment when the cork is withdrawn, and crystallisation is occurring, it will be felt to grow warm ; or, still better, if a

thermometer be quickly introduced, it will be seen to rise through 16° or 20° .

183. The experiment just recorded is a striking illustration of the general law, that as all solids, in becoming liquids, render a large amount of heat latent, so all liquids, in becoming solids, evolve or render free a large amount of heat previously latent.

184. A variety of simple but instructive experiments may likewise be made in illustration of the fact, that when a solid is compelled to liquefy rapidly, without heat being freely supplied to it, so as to confer on it liquidity, it lowers the temperature of surrounding objects by depriving them of their heat. Thus, there is scarcely one of the salts, such as common salt, Glauber's salt, nitre, and the like, which does not lower the temperature of water when dissolved in it, in consequence of the water determining the liquefaction of the salt, which, in its turn, forces the water to part with heat, in order to melt it. Thus, a handful of nitre thrown into water causes its temperature to fall about 9° ; sodic sulphate, dissolved in muriatic acid, lowers the thermometer 28° ; when snow is mingled with salt, the former melts with such rapidity, in consequence of its affinity for the salt, that the temperature sinks to -17° .

185. Such combinations go generally by the name of freezing mixtures, and are employed in summer to produce ices for the table.

186. The salt called calcic chloride, when mixed with snow, produces, whilst melting the latter, a cold sufficient to freeze mercury, which requires, before it congeals, to be reduced to the temperature of -38.9° .

Latent Heat of Vaporisation.

187. It is matter of familiar observation that most liquids, such as water, when exposed to heat, steadily rise in temperature till they reach a certain point, when the phenomenon of ebullition or boiling occurs, and the liquid passes away abundantly as an invisible gas or vapour.

188. It is not essential to the production of vapour that the

liquid should boil. No phenomenon is more familiar than the drying up of even large pools of water by silent conversion into vapour. The phenomena, however, we are about to explain are best observed with boiling liquids.

189. We have already referred, whilst describing the thermometer, to the fact, that so long as water, exposed to heat, continues boiling, a thermometer plunged in it stands at the same point—that, namely, marked on our thermometers as 212° F., or 100° C. We now add the statement, that the steam issuing from the boiling water has also the temperature of 100° , as we saw formerly that the water flowing from melting ice has the same temperature as the unmelted ice.

190. As the steam, then, is no hotter than the water, we may be tempted at first to imagine that nothing more is necessary, in order to convert water into vapour, than to raise it to the temperature of 100° . If this were all, however, that were requisite, the boiling of water would be a most perilous experiment; for, the moment the liquid rose to 100° , it would explode into steam with a violence exceeding that of ignited gunpowder. That this would be the case is certain, from the fact, that a given volume of water, when it changes into steam, occupies a space 1694 times greater than it does when liquid. In other words, 1 litre of water yields 1694 litres of steam. The strongest engine-boiler would be shattered to fragments by the instantaneous dilatation within it of even a small quantity of water.

191. Again, if vapours contained no more heat than the liquids which yielded them, they could not retain for a moment the condition of invisible gases, but would condense into liquids the instant they came in contact with any body lower in temperature than themselves. So far, on the other hand, are they from readily condensing, that in steam-engines, distilleries, and other places where it is essential to condense vapours, it is found necessary to expose them to a great amount of cold, otherwise they retain their condition as gases.

192. The explanation of these phenomena is furnished by

the fact, that as ice, in becoming water, renders latent a large amount of heat, water does the same in becoming steam. What occurs with water occurs with every other liquid. In every case, the volume of the substance is considerably increased in becoming a gas, and the force required to drive the particles asunder is the equivalent of the heat which becomes latent.

193. A few experiments will suffice to demonstrate the disappearance of heat during the conversion of liquids into vapours. If a vessel of ice-cold water be placed over a steady source of heat, and the time be observed which elapses before the liquid rises from 0° to 100° , it will be found that a period about five times longer transpires before the water is entirely boiled away. Now the water acquired 100 units of heat during the first space of time, which we may suppose to be half an hour, and during each of the five succeeding half-hours it must have been receiving the same amount of heat, or altogether five times 100—that

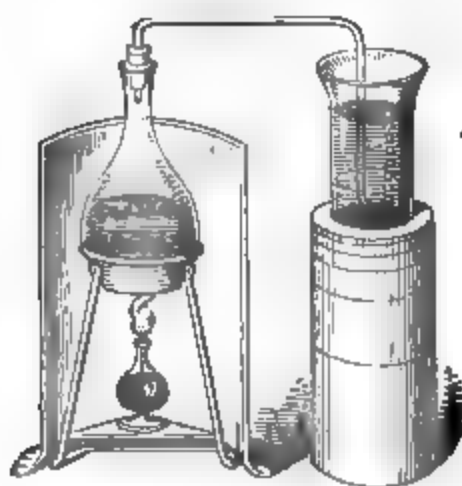


Fig. 17.

is, 500 units of heat; yet its temperature has never been higher than 100° , so that the heat must have been expended in some other way than in elevating the temperature. That it has entered into the steam, and become latent there, is demonstrated by condensing the vapour, and observing how much sensible heat it evolves; for as the heat which was latent in the liquid becomes sensible when it returns to the solid

state, so the heat which apparently disappears when water becomes steam, recovers its power to communicate warmth, and to expand the thermometer, when the steam returns to the state of water.

194. The most convincing way of illustrating this is the following: Let a tube from the mouth of a kettle or glass flask (see fig. 17), containing water kept boiling, be made to dip below

the surface of ice-cold water, so that the latter shall condense the steam; the steam, in passing through, will elevate the temperature of the water as it condenses in it, and speedily raise it to the boiling-point.

195. If 53 grammes of water at 0° be raised in this way to 100° , its weight will be found increased to 63 grammes, in consequence of the condensation of the steam.

196. Ten grammes, then, of water in the form of steam have raised 53 grammes of liquid water from 0° to 100° , so that each gramme of the liquid has received 100° of heat, and yet the (condensed) steam has not decreased in warmth, for it still retains the temperature of 100° , only it has ceased to be steam, and become water.

197. Let a similar experiment now be made with 53 grammes of ice-cold water, and 10 grammes of water (instead of steam) at 100° . On mixing the hot and cold water, the temperature will be found to rise about 16° . Hot steam, then, contains much more heat than equally hot water, and the former, in consequence, gives a much more severe scald than the latter.

198. In the first experiment, 10 grammes of water in the form of steam heated 53 grammes of water through 100° , so that one gramme of steam would raise to that temperature 5.3 grammes of water, or 1 gramme of water through $(100 \times 5.3 =) 530^{\circ}$. In other words, the steam of boiling water contains, in a latent condition within it, or, more strictly speaking, is capable of giving out, as much heat as would raise its temperature 530° , if it were sensible.

199. The following is a short table of the latent heat present in different vapours:

| Equal Weights. | Latent Heat of Vapour. |
|------------------------|------------------------|
| Water..... | 530 |
| Alcohol..... | 202.4 |
| Ether..... | 90.4 |
| Oil of Turpentine..... | 68 |
| Oil of Lemons..... | 80 |

200. Solids, we have seen, when quickly liquefied, produce

cold ; liquids, when quickly vaporised, do the same, and for a similar reason. Thus, if a readily vaporisable liquid, such as sulphuric ether or alcohol, be poured upon the hand, a sensation of cold is produced, in consequence of the liquid, compelled as it is to become vapour, robbing the hand of the heat it requires to render latent, before it can assume the gaseous form.

201. Water is sufficiently volatile to exhibit this phenomenon, as every bather must have experienced ; and many curious experiments can be shewn in illustration of this property. Thus, a small portion of water may be frozen by immersing a tube containing it in a wider vessel holding sulphuric ether, and compelling the ether to vaporise rapidly by placing it under a bell-jar on the plate of the air-pump, and withdrawing the vapour as fast as it forms by working the pump.

202. The ingenious apparatus devised by Dr Richardson, for producing local insensibility to pain in surgical operations, depends on the same principle. By it a blast of air charged with ether spray is directed on the place, and the rapid evaporation of the ether, from its finely divided condition, produces cold enough to numb the flesh. Water may readily be frozen in a test-tube by this apparatus.

203. Water may even be frozen by its own evaporation. For this purpose it is placed in a shallow, porous vessel, in the air-pump vacuum, above a wide basin containing strong oil of vitriol. The air is then withdrawn, and the whole left at rest. A portion of vapour instantly rises from the water, and fills the empty bell-jar standing on the air-pump plate. This volume of vapour, however, is immediately condensed by the oil of vitriol, which has a great affinity for water. Successive volumes of water-vapour rise in like manner, and are in turn condensed ; but the process does not proceed long before a cake of ice is seen in the porous vessel. The explanation is simple. The water having had nothing else to take heat from, takes it from itself, at least in part. It contains heat enough to maintain it all as a liquid, or to convert a portion of it into vapour, whilst

the rest becomes solid. The oil of vitriol promotes the formation of vapour by absorbing the vapour as fast as it is produced, and the vapour compels the unvaporised water to part with its heat to it; but in so doing, the residual liquid of necessity becomes solid.

204. We have stated already that there is no essential distinction between a gas and a vapour. The statement will be better understood now, after the exposition of latent heat. Our air is in greater part a mixture of two gases, oxygen and nitrogen, which we do not see condense under any circumstances, only, however, because we are not able, by any reduction of temperature, to deprive them of their latent heat.

205. Other gases, however, which were long reputed to be as little liable to alteration in condition, have been condensed into liquids, and frozen into solids. Carbonic dioxide presents the best example of this curious fact. It may be reduced to the liquid form in two ways: by compressing it into a very small space, it may be compelled to abandon its latent heat, which becomes sensible—the gas at the same time liquefying; or it may be exposed in suitable vessels to great cold, which in actual practice is a much less convenient plan; or compression and reduction of temperature may be simultaneously had recourse to, which is the process generally followed for the condensation of gases.

206. A liquefied gas is always a very volatile body, and may often be in part solidified or *frozen* by permitting the liquid to evaporate spontaneously. Thus, liquid carbonic dioxide, if allowed to evaporate rapidly, behaves exactly like water confined in the air-pump vacuum along with oil of vitriol. One portion of the liquid becomes gas, the other changes into solid carbonic dioxide, a substance scarcely distinguishable in external characters from snow.

207. Some gases, such as nitric tetroxide, cyanogen, and ammonia, do not require this process, but, by mere reduction in temperature, may be frozen like water. In short, the great majority of the gases comport themselves exactly as the vapours

evolved by liquids do—the difference between them being only one of degree, so that a greater amount of cold is required to condense the gas than to condense the vapour. This, however, implies no greater difference between a gas and a vapour than between two vapours, one of which contains a greater amount of latent heat than the other, or requires a greater reduction of temperature to render it liquid.

208. Some gases, such as oxygen, nitrogen, and hydrogen, have as yet resisted every attempt to liquefy them; but we do not doubt that this is only because they are the vapours of bodies so highly volatile, that we are not able to command a temperature low enough, or a pressure sufficient to induce them to part with their latent heat.

DISTILLATION.

209. The process of distillation, which depends upon the property possessed by many substances, of changing their state, without chemical decomposition, under the influence of heat, is made use of by the chemist for at least two purposes.

(1.) To free a liquid or solid from non-volatile impurities; as in the case of water and hydric nitrate.

(2.) To separate from each other liquids of different boiling-points; as in the process for obtaining alcohol from fermented liquors.

A very effective apparatus for distillation is represented in fig. 18. A is a vessel of glass with a curved neck, called a retort, into which the liquid to be distilled is introduced through an opening at the top. This vessel is heated by the lamp below it, and the vapour evolved from the boiling liquid passes down the neck and through a long tube, BB, the lower extremity of which enters a flask, D, called the receiver. Round the tube, BB, is fitted a larger tube, CC, secured by a perforated cork at each end, so that a space of not less than 1 cm. is left between the two tubes. Through this space a constant current of cold water is made to flow from the reservoir, E, or other water supply, and the waste water is

received in a vessel, F, or conducted down the sink. The vapour, in passing through the tube, BB, is cooled down and

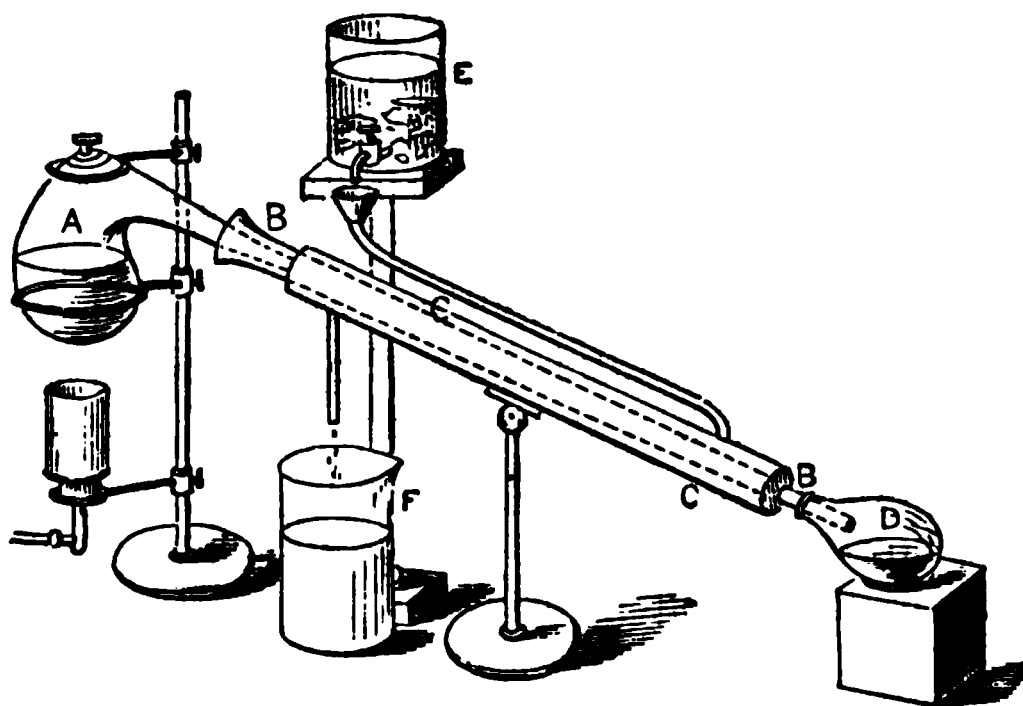


Fig. 18.

condensed into a liquid which collects in the receiver. This arrangement of condenser is termed a Liebig's condenser, from the great chemist who invented it.

210. For many purposes, where the product of distillation is not very volatile, a sufficiently complete condensation may be obtained by wrapping the neck of the retort (which must be a long one) in a fold of blotting-paper, kept wet by allowing cold water to drop continually upon it from a funnel, the neck of which is partially plugged with tow. The water which drips from the lower end of the paper is prevented from passing into the receiver, and guided into the vessel placed to receive it by a piece of tow or lamp-cotton twisted round the neck, and hanging down 10 or 12 cm.

211. When liquids differing in volatility have to be separated, a thermometer is introduced into the retort through the opening at the top, and the heat is so regulated as to keep the liquid gently boiling. When the thermometer is observed to be no longer stationary, but to rise above the boiling-point of the more volatile liquid, the receiver is changed, and the distillation then proceeded with. This is called fractional distillation; and

although it is difficult to effect a complete separation of several liquids by its means, it is continually employed in organic chemistry in the examination of complex mixtures, such as the oils obtained from coal-tar. The same apparatus will serve also for the purpose of taking the boiling-point of a liquid.

212. The distillation of a solid substance is termed 'sublimation,' and is usually effected by a much simpler apparatus than that above described. Thus, in the purification of crude sal-ammoniac, the rough product is placed in a large iron pan, over which a dome-shaped iron cover is fitted. The lower pan is strongly heated, and the salt sublimes into the cover, sufficient cold for condensation being obtained by allowing free access of air to its external surface.

CHAPTER VI.

LIGHT.

213. The influence of light in determining the chemical changes which take place in growing plants, and its applications in photography, have been alluded to in the introductory chapter, and will be explained more in detail under the head of Carbonic Dioxide and Silver. It is not proposed here to do more than give a short account of certain physical properties of light which recent discoveries have rendered most interesting to the chemist.

214. Light, like heat, is believed to consist in vibrations of the ultimate particles of matter. These vibrations form waves like those of the sea, propagated, not by actual onward motion of the particles, but by communication of motion from particle to particle. To illustrate this mode of propagation, let a long cord be laid on the ground, one end being retained in the hand. Then, by an up and down motion of the hand, a series of waves may be caused to run along the cord, each of its particles taking up in succession the up and down motion communicated to the end particle by the hand. So with light, the particles of a transparent substance take up the vibrations communicated to them by the particles of the source of light, and transmit them, more or less modified, to the more distant surface.*

* The hypothesis of an ether pervading space is not insisted on here. It does not seem to be proved that the particles of substances are incapable of transmitting light-motion; and it appears a step in the wrong direction to encumber science with an unnecessary hypothesis. See the preface to Brooke's *Elements of Natural Philosophy*, and Grove's *Correlation of Physical Forces*.

215. We are accustomed to take a ray of the sun as our typically perfect and simple light. But it is found not only that sunlight is made up of a vast number of vibrations, or light-waves, differing in length, but also that it is deficient altogether in a certain number of waves.

216. This is proved in the following way: A pencil of sunlight, S, is admitted into a darkened room through a narrow horizontal slit in the window-shutter, and allowed to fall on a white screen at a distance of two or three metres at least

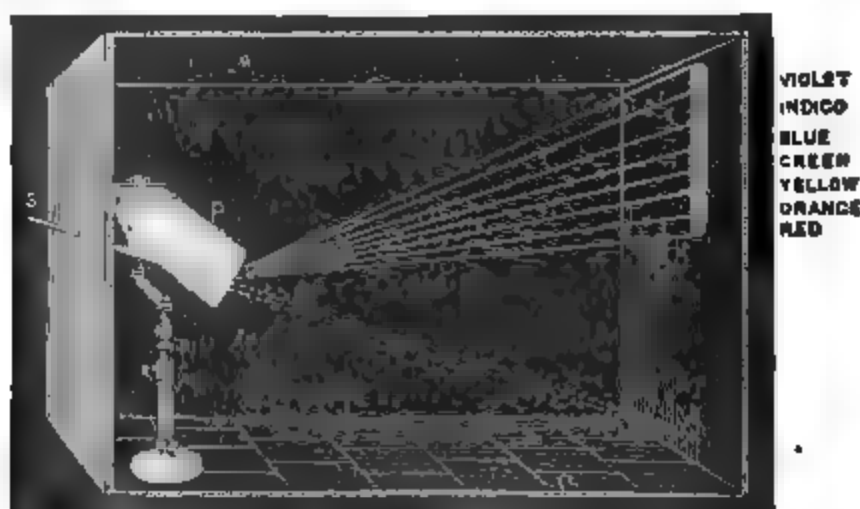


Fig. 19.

(H, fig. 19). A round spot of light (an image of the sun, in fact) will be seen at A. Now, if a triangular bar of glass, P, called a prism, is held in the position shewn, between the slit and the screen, the light is bent out of its direction towards the upper part of the screen. Moreover, we no longer observe the image to be a round spot of white light, but a long band of different colours ranged in the order shewn in the figure.

217. We thus learn that a sunbeam is composed of several constituent rays, which are bent out of their course, or *refracted*, unequally by the prism, and hence appear ranged side by side on the screen. Each of these elements, as we may term them, or ultimate constituents of the light, is a wave series, differing from the rest in its length of vibration. The extreme red ray, for example, is a set of waves, of which there are 1470 in a

millimetre ; while a ray in the violet consists of waves, of which there are 2270 in a millimetre.

218. If, in the next place, we form, not an image of the sun itself, but an image of the slit illuminated by sunlight, which we may easily obtain by placing a lens (a common magnifying-glass of rather long focus will do) between the slit and the prism, we gain a further insight into the character of sunlight. We have now upon the screen a multitude of images of the slit or line of sunlight, one corresponding to each element of the ray ; and we see at once (if the prism is a good one), that there are certain elements wanting—that there are gaps, or lines of no light, in the band, or spectrum, as it is called. These dark lines were first carefully observed and measured by an optician named Fraunhofer, of Munich ; and they are still called after him Fraunhofer's lines.

219. If, instead of the sun, a flame of coal-gas, a white-hot ball, or other incandescent substance, is used to illuminate the slit, we obtain a spectrum in which there are no dark gaps at all ; and we may naturally ask why the light of the sun, which we believe to be due to incandescent matter, should be deficient in certain rays. We gain the first clue to the answer by placing behind the slit, illuminated by a gas flame, a bottle filled with a coloured gas called nitrogen tetroxide. We then see the continuous spectrum actually furrowed by dark lines. The gas has absorbed certain ray elements ; and it is easy to infer that some such absorbing medium may exist between us and the sun.

220. Before inquiring into the nature of this medium, let us examine the character of the light emitted by other highly heated bodies than the sun or a gas flame. When some common salt is dissolved in alcohol, and the solution burned in a spirit-lamp, the flame is intensely yellow to the eye. If this flame is placed in front of the slit at S, we observe on the screen, not a variously coloured band, but a single broad line of yellow light. Instead of the spirit-lamp, we may use the flame of a Bunsen burner, in which a piece of platinum wire,

dipped in powdered sodic carbonate, is held, and we shall observe that this and all other compounds of sodium give the same yellow line of light, and nothing more; in other words, they emit light consisting of vibrations of one length only, or nearly so.

221. A more convenient arrangement for examining the light derived from various sources is shewn in fig. 20, and is called

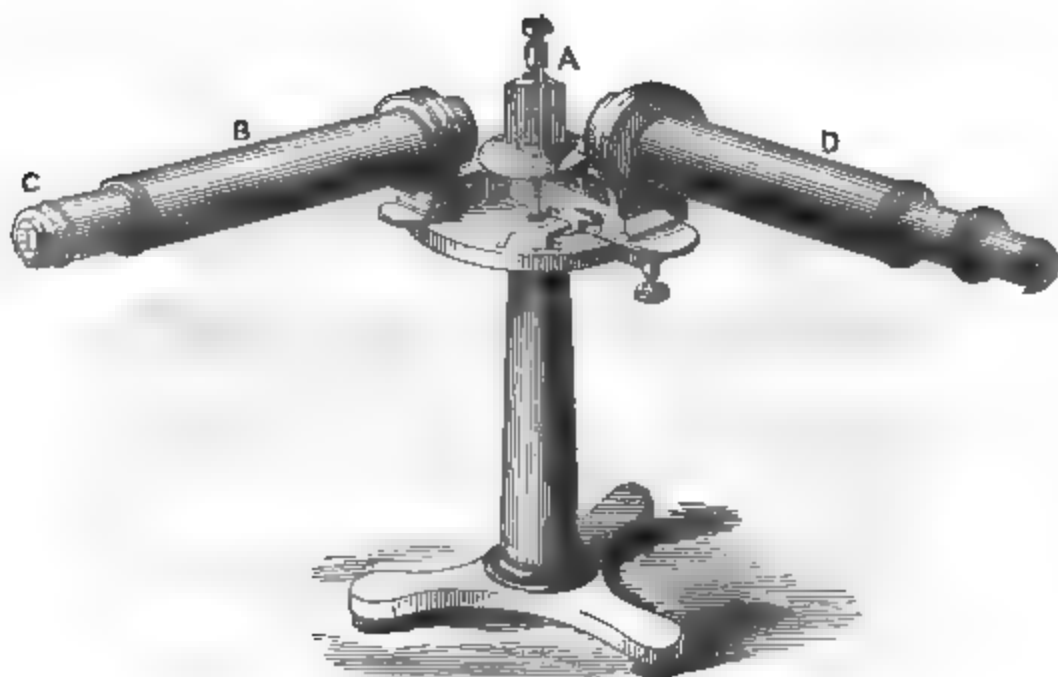


Fig. 20.

a spectroscope. It consists of a firm stand on which the prism A is fixed in a vertical position. On one side is attached a telescope B, the eye-piece of which is replaced by a frame C, containing two brass plates, the edges of which can be brought near each other by a screw, so as to form a narrow slit. On the other side is a similar telescope D, which is movable round a centre underneath the prism, and which is furnished with the usual eye-piece. The light passing in through the slit is refracted into a parallel beam by the object-glass of the first telescope, and then falls on the prism. The dispersed rays are taken up by the second telescope, and are seen by an observer in its field of view, as it is gradually moved round the centre. A

black cloth, thrown loosely over the prism and telescope, serves to shut out extraneous light, and thus we have all the advantages of a dark chamber.

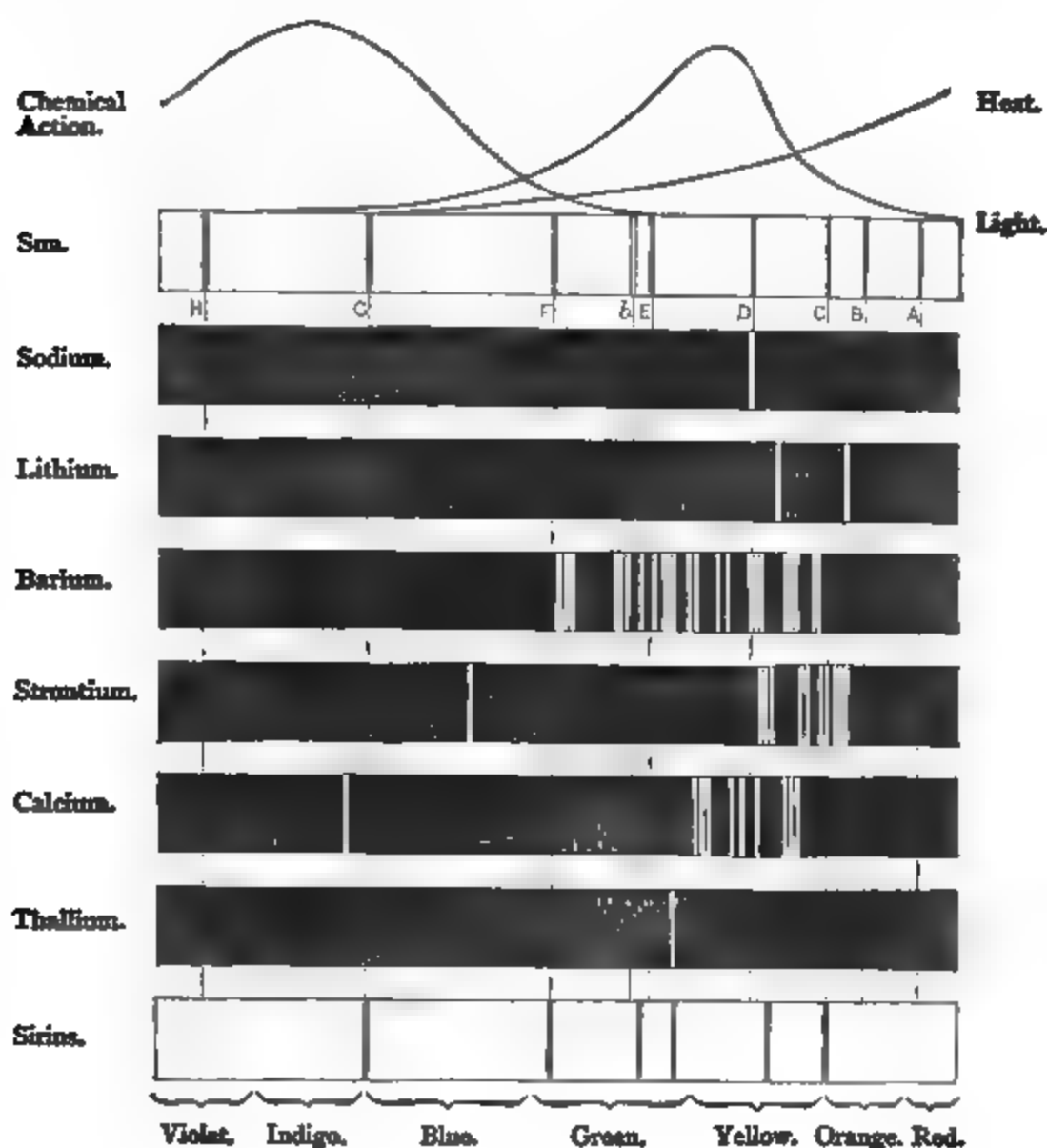


Fig. 21.

222. If we examine, by such an instrument, the light emitted by various substances when vaporised in the flame of the blow-pipe or Bunsen burner, we find that scarcely any element gives so simple a spectrum as sodium, but that each gives its own perfectly characteristic set of bright lines. A few of these

spectra are given in fig. 21, and will be noticed more fully under the head of the different elements. In the meanwhile the extreme delicacy of this method of qualitative analysis (which we owe to MM. Bunsen and Kirchhoff of Heidelberg) should be noticed. So small a quantity as one millionth of a milligramme or less of sodium may be detected by the appearance of the yellow line in the spectrum of a substance; and if a perfectly clean platinum wire, which of itself imparts no colour to the flame, be passed between the fingers, the yellow sodium flame will be seen when the wire is again brought into the flame.*

223. Let us now return to the subject of solar light. On an examination of fig. 21, it will at once be noticed that the bright line given by sodium exactly corresponds in position to a dark line in the solar spectrum; in other words, incandescent sodium emits a certain ray which is wanting in sunlight. The same is true of some other metals, such as barium, calcium, iron, copper, zinc, hydrogen, the spectra of which consist of bright lines corresponding to gaps in the sun's light.

224. It is impossible to avoid the conclusion that the above are not mere coincidences, but that there is a real connection between these metals and the materials of which the sun is composed, and MM. Bunsen and Kirchhoff have given what is, in all probability, the true explanation of the facts. They discovered that a vapour, below its point of incandescence, absorbs precisely those rays of light which it emits at a higher temperature. Thus, if a piece of sodium is volatilised in a tube, and the light from a luminous gas flame, or ignited cylinder of lime, is caused to pass through this vapour before it falls on the prism, a black line appears in the previously continuous yellow portion of the spectrum; and this line coincides in position with the bright yellow line emitted by the same vapour when heated more strongly.

225. The obvious inference is, that between us and the sun,

* In a powerful spectroscope, the sodium spectrum is seen to consist of two lines separated by a small interval.

and surrounding the latter, there is a stratum of comparatively cool sodium vapour which cuts off from us a ray which the white-hot body of the sun emits. We may reproduce these conditions on a small scale as follows: A piece of sodium is placed in a deflagrating cup, heated until it begins to burn in the air, and then immersed in a jar of oxygen. It burns with a brilliant light, and if this light is examined by the spectroscope, we observe a continuous spectrum crossed by a black line in the yellow. The intensely heated nucleus of sodium emits light of all colours, which in passing outwards has to traverse sodium vapours which are cooler in proportion as they are further from the centre of combustion, and consequently absorb their own yellow ray. These are precisely the conditions occurring near the sun's surface; and what is here said of sodium may be equally said of the other metals, barium, iron, &c., above mentioned. The conclusion drawn from the whole is, that the sun is composed of various strata of heated vapours incandescent near the centre, and becoming cooler and cooler, and hence absorbing definite portions of light as they are further from the incandescent strata.

226. After the constitution of the sun was thus determined with a probability approaching to certainty, it was natural to apply the same method of research to the other heavenly bodies. The planets are found to give the same spectra as the sun, with a few additional dark lines; and hence it is inferred that their light is reflected sunlight, some additional absorption having taken place in their own atmospheres, just as many additional dark lines appear in the solar spectrum when the sun is near setting, and its light passes through a greater thickness of our own atmosphere. The stars give spectra containing dark lines, some of which, but not all, coincide with the bright lines in the spectra of known elements. A few of the lines in the spectrum of Sirius are shewn in fig. 21, and it seems proved that hydrogen, sodium, and magnesium are present in this almost immeasurably distant star. But perhaps the most remarkable result has been obtained with respect to the nebulae. It was believed that all

of these were star-clusters, only appearing as luminous haze because our eyes and telescopes were not powerful enough to separate them into their component stars. But an examination of the light emitted by the nebulae has led to their division into two classes: (1.) Those which give spectra resembling those of the stars and sun, and which are hence probably aggregates of stars, according to the old theory; (2.) Those which give spectra consisting of only a few bright lines, and which are inferred to be masses of glowing gas, apparently in some cases hydrogen and nitrogen, without any cooler atmosphere outside these to cause absorption.

227. But the spectroscope has done more than enable us to discover the constitution of celestial bodies; it has taught us that beneath our feet there lie elements, the existence of which was unsuspected. In the year 1859, Professor Bunsen, when examining the residue obtained by evaporating the water of a German mineral spring, found that it gave, when ignited, a spectrum which contained bright lines not corresponding to those obtained from any known substance. He followed up this discovery, and succeeded in isolating two new elements, which he named caesium and rubidium, the spectrum of the former characterised by two blue lines, that of the latter by two red lines. Shortly after, Mr Crookes observed a bright green line in the spectrum of a residue from a German chemical manufactory. The position of this line is shewn in fig. 21, and it was soon discovered to be due to a new element, to which the name 'thallium' was given. All these elements have, since their discovery, been proved by the spectroscope to be present in a great number of substances. Thus, rubidium has been found in many mineral springs, as well as in tobacco, coffee, and beet-root; and thallium occurs in many specimens of pyrites, and in some sandstones. Still more recently, another element, named indium, has been added to the list of spectroscopic discoveries.

228. Enough has been said to give an idea of the enormous importance of this new method of chemico-physical analysis.

Every year brings before us new applications of it—to the manufacture of steel by Bessemer's process, to the examination of colouring matters, to the detection of blood-stains. But, for more detailed information, the student must be referred to Roscoe's *Lectures on Spectrum Analysis*, or the article on Spectrum Analysis in Watts' *Dictionary of Chemistry*.

CHEMICAL ACTION OF LIGHT.

229. It has been mentioned in Chapter I. that sunlight has considerable powers of producing chemical decomposition and combination. But, now that we have learned that sunlight is an aggregate of many different rays, it will be interesting to inquire whether all these rays have the same power of effecting chemical change, and, if not, what rays are the most active.

230. If a piece of paper, coated superficially with a silver salt such as the chloride, is held in the spectrum of sunlight, it is observed to blacken, in consequence of chemical decomposition, only where exposed to the green and blue rays, the maximum effect being produced at a point even beyond the visible violet rays, while in the yellow and red rays the silver compound remains almost wholly unaffected. Again, if a glass bulb, filled with a mixture of hydrogen and chlorine, is held in the red rays, no change takes place; but, if held in the blue rays, the gases at once combine with explosion.

231. We are thus able to construct a curve such as is shewn at the top of fig. 21, which represents the intensity of chemical action shewn by the various rays. Two other curves are also introduced, indicating the position of the maximum luminosity and heat in the spectrum.

232. It has been proved by the experiments of Bunsen and Roscoe that in the above chemical changes a quantity of light disappears by absorption, proportional to the amount of change effected. Light-force is, in fact, converted into chemical force, none of it being lost.

233. When a healthy growing plant is exposed for some

time to the sun's rays in a jar filled with carbonic dioxide, the jar will be found to contain a considerable amount of oxygen gas, an equal volume of carbonic dioxide having disappeared. The light-vibrations have been absorbed by the green colouring matter of the plant, conferring on it the power of decomposing carbonic dioxide into its constituents, carbon and oxygen, the former being retained by the plant. That it is really the light which has caused the change, is shewn by the fact, that no such decomposition occurs in darkness; but it is a question yet undecided whether this decomposition goes on most actively under the violet or under the more luminous rays. Both, however, seem to be necessary for the full development of plant life.

CHAPTER VII.

ELECTRICITY.

234. That mode of force which we call electricity is, in some respects, the most powerful agent of decomposition which the chemist possesses. It will be treated of here solely in its relations to chemistry, and hence only a limited reference will be made to that manifestation of it which is obtained from an electrical machine, and is known as frictional electricity, and which has comparatively slight powers of effecting decomposition.

235. There do not appear to be such clear and definite conceptions of the nature of electricity as of the nature of light and heat. There is little room for doubt that it consists of some kind of molecular motion; not, it would seem, of wave-motion, but perhaps of a motion of revolution of the molecules round axes which lie in the same direction, like the bobbins of a cotton-mule.

236. It is pretty certain that, while a body is under the influence of electricity, its particles are in a state of constraint. The intimate connection of electricity with magnetism, the tendency shewn by bodies to place themselves, when freely suspended, in a definite position with respect to a wire transmitting electricity, and the remarkable change produced in a ray of light when passed through a block of glass round which electricity is made to pass, are all proofs of a disturbance of molecular arrangement; and there is no difficulty in conceiving

that, for the time, the molecules have their axes of rotation rendered parallel. In such a case they are said to be 'polarised.'

237. Although, in what follows, the term 'current of electricity' will be employed for convenience and clearness of illustration, yet it is not intended to imply that any actual fluid is transmitted, but only that this peculiar state of polarisation is rapidly communicated from particle to particle. This polarisation is produced in some bodies with much greater facility than in others. Bodies which belong to the former class, such as the metals, are said to be 'good conductors;' bodies which belong to the latter class, such as glass and most gases, are called 'bad conductors' of electricity.

238. When a plate of zinc and a plate of platinum, about 7 or 8 cm. square, are immersed, at a little distance from each other, in a vessel of diluted hydric sulphate (oil of vitriol), or of any other liquid which acts more strongly upon the zinc than the platinum, the two metals are thrown into opposite polar conditions.* These states differ from each other much in the same way as the north and south poles of a magnet; and just as when a piece of iron is made to form a communication between the poles, it acquires properties which it did not possess before, so, if the zinc and platinum are connected by a metallic wire (fig. 22), or any other conductor, the latter acquires new properties, which we express by saying that a current of electricity is passing along it.

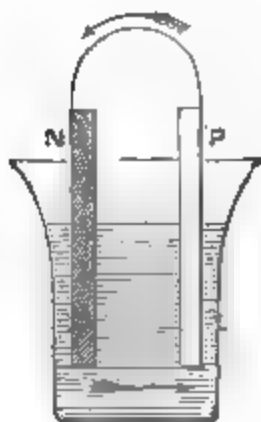


Fig. 22.

* The zinc plate used for this experiment should be either of pure zinc, or (since the pure metal is expensive and difficult to obtain) it should be covered with a coating of mercury. This may be easily done by placing the zinc for a few seconds in some diluted hydric sulphate to clean it, and then pouring upon it a little mercury, and spreading the latter over the surface with a cork until a uniform bright coat of amalgam is formed. The mercury is not acted upon by the dilute acid, and it protects the impure metal from solution as long as the electrical current is not completed, while it does not interfere with the action of the acid when the current of electricity is passing. A plate of zinc thus treated is said to be amalgamated. The dilute acid mentioned in the text may be made by mixing gradually 100 c.c. of the strong acid with a litre of water.

239. For the sake of clearness, let us suppose that the current flows from the copper to the zinc in the direction of the arrow. Then the point P, at which it leaves the platinum, is called the 'positive pole;' and the point N, at which it reaches the zinc, is called the 'negative pole.' The same supposition is made respecting the electricity in the vessel itself. It is said to start from the zinc, which is therefore called the 'positive' metal, and to proceed through the liquid to the platinum, which is called the 'negative' metal. In general, if we place ourselves at any point in the circuit, the point from which the current is defined to come, is called the positive end; the point towards which the current goes, is called the negative end.

240. Let us now briefly examine the new properties gained by the wire thus forming part of the electric circuit.

(1.) It will become heated; the rise in temperature being dependent on the size of the wire and the material of which it is made. A thin wire becomes hotter than a thick wire; and a wire of platinum becomes hotter than a silver wire of the same diameter. The development of heat is proportional to the resistance offered by the wire to electrical motion, and silver is a much better conductor of electricity than platinum. If the wire is very fine, light as well as heat will be produced; the wire becoming white-hot and even melting.

(2.) When the wire (which, for this and the following experiments, should be of copper) is placed north and south, the positive pole being northwards, and a compass is brought close over it, the magnetic needle is deflected, its north pole moving westwards. A similar movement, but in the opposite direction, is observed when the needle is placed below the wire. The general result is expressed by saying, that a magnet tends to place itself at right angles to a wire conveying an electric current.

(3.) If the wire is dipped into fine iron filings, they will be attracted by it, shewing that it has itself acquired magnetic properties; and if it is coiled round a bar of soft iron covered with a fold or two of paper, so that the coils do not touch each

other, and the current is compelled to traverse the whole length of the wire, the soft iron becomes a strong magnet.

(4.) If the wire is cut at any point, and the two ends are dipped into a strong solution of cupric sulphate (blue vitriol), metallic copper is deposited as a bright red coating upon the negative end, and the positive end, if it is of copper, is slowly corroded and dissolved. All these effects cease as soon as the circuit is interrupted.

241. While the circuit is complete, it will be found that chemical action is going on in the vessel in which the zinc and platinum plates are immersed. The zinc is being dissolved by the acid, and bubbles of a gas, which may be proved to be hydrogen, are given off from the surface of the platinum. This action on the zinc, if the metal is pure or amalgamated, only goes on while the current is passing, and the amount of zinc dissolved is strictly proportional to the amount of work done by the current, whether in producing heat, magnetism, or chemical action. Thus, for every 65 milligrammes of zinc which have been dissolved, it will be found that 63.4 milligrammes of copper are deposited on the negative pole.

242. The arrangement above described is termed a single-cell battery. Its effects are comparatively feeble, not merely because only a small quantity of electrical separation can take place, but chiefly because of the resistance offered by all substances, more or less, to the passage of the current. We may liken the passage of an electric current through a long thin wire, or a stratum of a badly conducting liquid, to the passage of a large army over a narrow bridge or a bad road. The men, and therefore the means, are there; but they cannot be brought to bear in such numbers on a given point in the same time as if the bridge were broader or the road smoother. So electrical force or motion is impeded, and even stopped altogether, by placing in its way a sufficiently bad conductor. Obviously, therefore, in order to obtain powerful effects in a short time, we must either diminish the resistance or increase the power of the current to overcome it—the electro-motive force or *intensity*,

as it is called. This may be done by linking together a number of single cells in such a way that the platinum of one cell is connected with the zinc of the next, and so on—the zinc plate of the first cell, and the platinum plate of the last cell, being connected by the substance through which the current is to be passed. The effect of this arrangement is, that the electromotive force in each cell is augmented by that of the adjoining cells, and we find that the accumulated intensity at the two poles is sufficient to overcome the resistance of a comparatively bad conductor.

243. It is usually said that the quantity of electricity is not increased by the number of cells. If by quantity is meant the amount of work, chemical or otherwise, which the current is capable of doing in a given time, the statement must be modified. Let us take the case of two cells, in each of which 65.2 grms. of zinc are being dissolved in an hour, the current being passed through a solution of cupric sulphate. Then, by the law of the conservation of force, the current developed must liberate twice 63.4 grms., or 126.8 grms. of copper, or do some equivalent of other work. But it only liberates 63.4 grms. of copper; the rest of the force being spent in overcoming the resistance of the copper atoms to separation (in lifting, in fact, a heavy weight) in a shorter time. We cannot obtain the same result by increasing the size of the plates in a single cell, chiefly because the resistance of the liquid in the cell is thus so far diminished that a portion of the current circulates in the cell itself, and is not available for external work. Hence it will not answer to place the series of plates in one undivided trough; each pair must be placed in its own separate cell. When a long series of cells is carefully insulated, effects are produced approaching to those of an electrical machine.*

* To illustrate the meaning of the terms *quantity* and *intensity*, as applied to an electric current, we may take the following comparison. Let the work to be done be represented by a cistern, to be filled with water. Then, the best means of doing it will depend upon the nature of the supply-pipe. If the latter is short and wide, then a full stream of water may be brought from a source scarcely above the level of the top of the cistern. But if the pipe is long, narrow, and obstructed by sand, then the water must be forced through

244. Of the various forms of battery available for chemical use, only two will be mentioned here. The power of a pair or a series of zinc and platinum plates, immersed in dilute acid, very soon decreases when the circuit is completed. This is due to the fact, that the hydrogen gas evolved at the surface of the platinum, adheres to it so strongly as to diminish the acting area of the plate, and thus increase the resistance (hydrogen being a very bad conductor). This evil may be remedied either by mechanical or by chemical means. Thus, we may alter the surface of the plate in such a way as to diminish the adhesion of the gas, which will then be given off as fast as it is produced. This is the principle of Smee's battery, in which the negative plate consists of a thin sheet of platinum or silver, upon which a layer of very finely divided platinum has been deposited. The surface is thus formed of a multitude of minute points, from which the hydrogen is evolved with great ease and rapidity. This plate is hung in a wooden frame, between two thick plates of amalgamated zinc; the whole being immersed in a jar of dilute hydric sulphate (1 measure of acid to 6 or 8 of water). This form of battery is very convenient for general use. It gives a fairly constant current for many hours, it is easily put in action, and no noxious fumes are evolved from it. Five or six cells, with plates about 14×8 cm., are sufficient for almost all purposes of experiment, except the electric light. But it is by no means so powerful as the battery next to be described, and which is called Grove's battery. In this the inconvenience of the adhesion of the hydrogen is avoided by placing the negative plate in contact with a liquid which is readily decomposed by hydrogen; the result being that the gas is not evolved at all, but is absorbed in the liquid itself. The liquid used is strong nitric acid (hydric nitrate), which is contained in a cell of porous earthenware, in which the platinum plate is immersed. This porous cell is placed within a U-shaped strip of sheet-

it in a thin stream by considerable pressure; for instance, by drawing it from an elevated reservoir. So, in an intensity current we have a considerable 'head' of electricity, so to speak, which is available for overcoming resistance.

zinc, the whole being contained in a jar of glass or vulcanite filled with dilute hydric sulphate. When the circuit is completed, the hydrogen, as above stated, decomposes the hydric nitrate, with formation of water and lower oxides of nitrogen. These latter at first dissolve in the liquid, but are eventually given off as the action continues; and the corrosive character of the vapours is the great drawback to this form of battery. The intensity of the current obtained is very great (although by no means constant), since the resistance within the battery is small; and 2 or 3 cells (with platinum plates about 12×5 cm.), are equivalent to 7 or 8 of Smee's construction.

ELECTROLYSIS.

245. It has been already mentioned that a solution of cupric sulphate is decomposed by an electric current. Such a decomposition by electricity is called 'Electrolysis,' and a very large number of liquid compounds and of salts in solution, are capable of undergoing it, and are hence called 'Electrolytes.' If, for instance, the current of a battery is passed through water, to which about $\frac{1}{12}$ th its volume of hydric sulphate has been added, the poles—or *electrodes*, as they are called—being plates of platinum not less than a square centimetre in area, the water is decomposed, 18 grms. of it yielding 2 grms. of hydrogen and 16 grms. of oxygen.* Fig. 23 shews a convenient apparatus for making this experiment. The neck of a large funnel is closed by a cork, through which the electrodes pass. Over each plate is

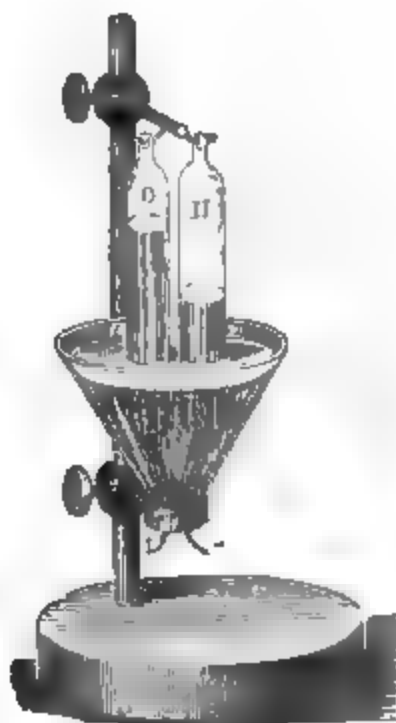


Fig. 23.

* The above is the usual statement with regard to the electrolysis of dilute hydric sulphate. But it is by no means clear that any water is decomposed under the circumstances. It would seem likely that the hydric sulphate alone is really decomposed, its hydrogen

suspended a tube about 2 cm. in diameter, filled with the dilute acid. Since the weights of equal volumes of hydrogen and oxygen are as 1 : 16, the observed result is, that the volume of hydrogen liberated is twice that of the oxygen.

246. Again, if the current is passed through a solution of sodic chloride, to which a little solution of reddened litmus has been added, the solution round the negative pole will turn blue; while that round the positive pole will lose its colour altogether. It will be an advantage, in this experiment, to place the solution in a beaker or tumbler, which is roughly divided into two compartments by a diaphragm of coarse blotting-paper. This will prevent the portions of the liquid round each pole from readily mixing. The same result is attained by using a wide U-tube (fig.

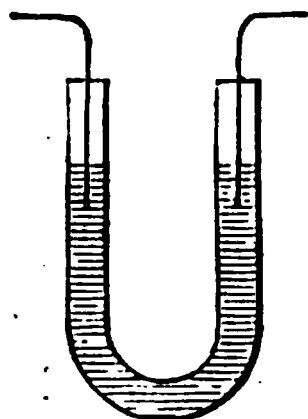


Fig. 24

24). It will be observed that gases are evolved at both poles; and the gas at the negative pole may be proved to be inflammable, and to possess the other properties of hydrogen; while the gas liberated at the positive pole is chlorine, which has the property of bleaching vegetable colours, and which, from its solubility in water, is evolved only in small quantity. In this experiment, the primary action of the current is to decompose the molecules of sodic chloride into sodium and chlorine. The latter is evolved in the free state, while the former decomposes the water at the moment of its liberation, forming sodic hydrate (which turns the reddened litmus blue) and free hydrogen.

247. It seems clear that in this and in all other cases of electrolysis there is no actual transference of the substances decomposed from one pole to the other, but all the intervening

going in one direction, and its sulphur and oxygen in the other. A portion of the oxygen is evolved as gas, while the rest remains in combination with the sulphur as sulphuric trioxide, which unites with the surrounding water to form hydric sulphate. If, however, the positive electrode is a fine wire, scarcely any oxygen at all is evolved, while the liquid round the electrode acquires oxidising powers which hydric sulphate does not possess. It is probable that in this case sulphuryl peroxide $(\text{SO}_2)_2\text{O}_2$, is formed, and this, like hydric peroxide, is gradually decomposed into a lower oxide and oxygen. Pure water can be decomposed by electricity, but a very powerful battery is required for the purpose.

molecules in the line of the current are polarised somewhat in the manner shewn below, Na representing a particle of sodium, and Cl a particle of chlorine :



The particle of sodium at the end of the row is liberated, the chlorine unites with the sodium of the next molecule, and so on ; the particle of chlorine at the other end being similarly set free. This alternate breaking up and reproduction of molecules of the salt is continued as long as the current passes. The following experiment may be given in support of the above explanation. If three glasses, filled with solution of sodic chloride tinged with red litmus, are placed in a line, and connected by pieces of lamp-cotton or tow soaked in the solution, and if the poles of the battery are placed, one in the first glass, and the other in the third glass, the colour of the litmus in the centre glass will remain unchanged. This would not be the case if free chlorine and sodium were actually passing through it in their way to their respective poles.*

248. When a series of different electrolytes—for instance, dilute hydric sulphate, stannous chloride, and plumbic iodide (the latter two in a state of fusion)—are placed in a row, and the same current made to pass through them in succession, it is found that a definite relation exists between the amount of decomposition effected in each case. Thus, for every 65 grms. of zinc dissolved in each battery cell, we have 2 grms. of hydrogen, 118 grms. of tin, and 207 grms. of lead liberated at the negative pole ; and 16 grms. of oxygen, 71 grms. of chlorine, and 254 grms. of iodine obtained at the positive pole. By extending the above experiments, we can construct a series of numbers expressing the relative weights of different elements, which can be obtained by means of the same quantity of electric force. These weights are, as may be seen from the above examples, identical with the weights of the elements which can

* The resistance to the current is here considerable, owing to the small area of the liquid saturating the lamp-cotton, and hence a pretty strong battery is required.

replace each other in a chemical compound. Thus, starting with 73 grms. of hydric chloride, which contains 2 grms. of hydrogen and 71 grms. of chlorine, when the chlorine is replaced by 16 grms. of oxygen, we obtain water; when by 254 grms. of iodine, we obtain hydric iodide; and if the 2 grms. of hydrogen are replaced by 118 grms. of tin, we get stannous chloride; if by 207 grms. of lead, we get plumbic chloride.

249. Such a series of numbers, which are called 'electro-chemical equivalents,' are in some cases identical with, in others simple multiples of, the atomic weights of the elements; and they afford good illustrations of the doctrine of replacement, or equivalency. For instance, we know of two compounds of copper with chlorine, both of which may be decomposed by the electric current. When the same current is passed through (1) hydric chloride, (2) cupric chloride, (3) cuprous chloride, it is found that for every 2 grms. of hydrogen liberated in (1), 63.4 grms. of copper are liberated in (2), and 126.8 grms. of copper in (3), the weight of chlorine obtained at the other pole being the same in all three cases—namely, 71 grms. Hence it appears that the same quantity of electric force is competent to liberate twice the weight of copper, when employed to decompose cuprous chloride, as when employed to decompose cupric chloride. But the amount of actual work done in the two cases must be equal, and we must infer that the element copper has two different 'equivalents'—that it is retained in combination with two different degrees of force. The relation of this to the subject of atomicities will be explained in a later chapter.

250. By a study of the results of electrolysis, we are enabled to arrange substances in two great classes. (A.) Those which are obtained at the positive pole, and which (on the principle that oppositely electrified bodies attract one another) are called electro-negative: such are oxygen, nitrogen, sulphur, chlorine, bromine, iodine, fluorine, cyanogen, &c. (B.) Those which are evolved at the negative pole, and are called electro-positive: such are hydrogen and the metals. This classification,

however, is not absolute. The same element may be obtained at either pole, according to the particular combination in which it occurs.

251. The same must be said of the relative position of each substance in the series, which varies according to the conditions of the experiment. We can determine this for any particular case by observing the direction of the current obtained when the substances to be compared are used as the plates of a battery cell. Thus, when a plate of silver and a plate of lead are immersed in dilute hydric sulphate, the current flows from the lead to the silver within the liquid. The lead is more acted upon by the dilute acid than the silver, and hence corresponds to the zinc of an ordinary battery, and is electro-positive towards silver. But, if the same two plates are immersed in a solution of potassic cyanide, the current flows in the opposite direction. The silver is here the more easily acted upon of the two, and is electro-positive.

252. If the liquid is of such a nature as to act upon both the metals placed in it, then, while the circuit is completed, the chemical action upon the negative metal is lessened, or even altogether stopped. Thus, diluted hydric nitrate can dissolve copper as well as zinc, but the latter more readily than the former. When the metals, however, are connected, either by being made to touch within the liquid or by an external wire, the copper does not dissolve at all, while the zinc dissolves more rapidly than if not connected with a more negative metal. It was on this principle that Davy sought to protect the copper sheathing of ships. Copper dissolves in sea-water; but if it is fixed by zinc nails, or if small pieces of zinc are attached to its surface, it remains totally unacted upon, while the zinc alone is dissolved. Iron, in the same way, is protected from rusting by a thin coating of zinc, as in the material called galvanised iron.

ELECTROTYPING.

253. This must be briefly noticed as a very important application of electro-chemistry. Since solutions are decomposed molecule by molecule, the particles of a metal deposited on the negative electrode form a film which adheres very closely to, and is an exact copy of, the electrode itself. In order, therefore, to obtain a fac-simile of a medal, a 'mould,' or reversed impression, is first made; and this is then placed as the negative electrode in a solution of a metallic salt, such as cupric sulphate. A coating of metal will be gradually deposited upon the mould, and this, when removed, will be found to be a faithful copy of the original medal. The details of the process cannot be entered into here, but the following hints may serve to suggest instructive experiments.*

254. (1.) *The moulds.*—A very good material for impressions of small objects, such as seals, is sealing-wax. A moderate quantity of this should be melted on a card, held at some height above a candle, and continually stirred with the end of the stick of wax. When it has cooled a little, the seal, after being breathed upon, should be brought down on it with some pressure, and left until the wax is quite cold and hard, when the seal should be carefully detached. Gutta-percha is another excellent material: it should be softened in hot water, moulded by the fingers into a ball, and then placed on a wetted plate, and the seal pressed into it, the pressure being continued until the gutta-percha is hard. An alloy called 'fusible metal,' which will be described under the head of Bismuth, is in many respects the best of all materials for moulds, but it requires some care to obtain good results with it. A little should be melted in an iron spoon over a lamp, and then poured into a saucer; the surface should be cleared from oxide, by passing a card lightly over it; and, as soon as the metal is observed to become pasty, the seal or medal should be dropped upon it from the height of

* The best practical treatise on the subject is Walker's *Electrotype Manipulation*, which is, however, unfortunately, now difficult to procure.

a decimetre or so. As this alloy has the property, like water, of expanding as it solidifies, very sharp casts are obtained. Since neither sealing-wax nor gutta-percha conducts electricity, the surface of moulds made of them must be covered with some conducting material, graphite (the common black-lead used for grates) being generally employed. The mould is breathed upon, or, if it is of sealing-wax, slightly moistened with alcohol; and the black-lead is applied by a soft brush until a good polish is obtained. Lastly, a piece of copper wire is heated, and pressed on the edge of the mould until it is partly imbedded, and a little more black-lead is rubbed over the part to make the connection good. Moulds of fusible metal must be varnished on the back and edges, to prevent the deposit of metal on those parts.

255. (2.) *The electrotyping apparatus.*—A single cell of Smee's battery is generally sufficient. The zinc is connected with the wire attached to the mould, and the platinised silver is similarly connected with a strip of sheet copper. The mould and the copper strip are then immersed in a jar containing a saturated solution of cupric sulphate, to which about $\frac{1}{20}$ th its volume of hydric sulphate has been added. The deposit of copper immediately commences on the parts near the wire, and gradually spreads over the mould; while the copper plate, which forms the positive electrode, is dissolved by the acid liberated upon it, and thus the strength of the solution is kept up.

256. Electrotypes may be readily made without the employment of a separate battery, in the following way. A round jar of porous earthenware (a common flower-pot will answer, the hole at the bottom being stopped by a cork) is filled with dilute hydric sulphate, and placed in a larger jar containing the saturated and acidified solution of cupric sulphate. The mould is attached by a copper wire to a strip of amalgamated zinc, and the latter is immersed in the acid, while the mould is placed in the outer jar, and speedily receives a deposit of copper. The nature of the action is the same as in the ordinary battery, the mould taking the place of the platinum or negative

plate, and the intervening particles being polarised in the following way :



The sulphur and oxygen at the surface of the zinc combine with the metal to form zinc sulphate, while the copper particle at the other end of the chain is deposited on the mould. It is necessary to keep up the strength of the copper solution by suspending in it a muslin bag containing crystals of cupric sulphate.

257. In order to obtain a good tough deposit of copper, there are several points to be attended to.

(1.) The temperature of the solution should not be low. In frost the action almost entirely ceases.

(2.) The intensity of the current must be proportioned to the strength of the copper solution. If the intensity is too great, or the solution is allowed to become weak, or contains much free acid, hydrogen as well as copper will be liberated on the mould, and the copper will appear as a dull, red, non-adherent powder. The same is likely to happen when the negative electrode is very small, as it always is at first when a mould coated with graphite is used, the action being concentrated on the wire and the adjoining parts. To avoid this, it is advisable to expose only a small surface of zinc to the acid at first; when the mould is nearly covered with copper, more acid may be poured into the jar in which the zinc is placed. One of the great advantages of using a separate decomposition cell is, that the copper dissolved from the positive electrode maintains the solution at a constant strength. If the simpler 'single cell' apparatus is used, crystals of cupric sulphate must be added from time to time, and it is best to place them near the surface of the solution in a wire gauze tray or a muslin bag. If the current is too weak, the copper will be deposited very slowly, and will be crystalline, hard, and brittle. Fresh acid should be put into the battery cell, or the porous jar containing the zinc,

and the solutions may be warmed. The general rule to be observed is, that the strength of the current should be maintained just short of the point at which gas is liberated with the copper.

258. In about a day and a half (or less in warm weather), the deposit will be thick enough to be removed by carefully loosening the edges from the mould. It may be strengthened by backing it up with soft solder, which will readily adhere if the surface of the copper is untarnished and is moistened with a little zinc chloride. The edges should then be trimmed with a file. Leaves, flowers, bunches of grapes, &c., may be coated with copper in a similar way, if black-lead is carefully rubbed over them. To preserve the lustre of the copper, they should be well washed, quickly dried, and varnished at once.

259. The processes of electro-plating and gilding are similar to that which has just been described, a moderately dilute solution of argentic or auric cyanide in potassic cyanide being used, to decompose which a higher battery power is required.

CHEMICAL EFFECTS OF THE SPARK CURRENT.

260. Of this mode of electrical motion very little can be converted into chemical action, the greater part passing into physical forces, such as mechanical and heat motion. Nevertheless, water may be decomposed by passing through it a spark current, the poles being fine platinum wires. Again, if a pointed slip of paper, moistened with a solution of potassic iodide, is held near a point attached to the conductor of an electrical machine so as to receive the silent discharge, not the spark, the end of the paper becomes brown, owing to the liberation of iodine. But the most remarkable effects are produced when the electric current is passed through gases. Thus a stream of sparks, when passed between platinum wires in a tube filled with ammonia gas, decomposes the latter completely into its constituents, nitrogen and hydrogen; and when passed in a similar way through dry oxygen gas, converts some of it into

that peculiar modification called ozone. Many other gases are decomposed by the current from an electrical machine or an induction coil, and the maximum effect is produced when the gases are passed between two oppositely electrified surfaces—for instance, between two plates of glass placed parallel, and about 3 or 4 mm. apart, the outer surfaces of which are coated with tinfoil, and connected with an induction coil. Under these circumstances no spark passes, but the intervening space is thrown into a state of violent molecular disturbance, and a peculiar glow is observed in the dark. It is difficult in some cases to distinguish between the effect of the heat produced and the effect produced directly by the current, either being competent to cause decomposition. But ozone cannot be produced—in fact, it is destroyed—by heat.

261. We may notice, in conclusion, the enormous amount of mechanical force which corresponds to a small amount of chemical action. Faraday inferred, from the results of his experiments, that more electricity was required to decompose a decigramme of water into its constituent gases, than was developed in the course of a violent thunder-storm. This gives us some idea of the magnitude of the force of chemical action, which we have next to consider.

CHAPTER VIII.

CHEMICAL AFFINITY.

262. We now come to a mode of force which it is more immediately the province of the chemist to investigate. The real nature of chemical affinity is very imperfectly understood. We can study its effects, examine the conditions under which it acts, and determine its equivalent in other forces; but we are as ignorant of the nature of the force itself as we are of the nature of gravitation.* What we do know is that, when certain substances are brought into actual contact with each other, they disappear, and a substance appears which differs, more or less, in properties from the original substances; and, moreover, that from this compound we can usually, by the employment of a certain amount of force, obtain again its elements, with their properties unaltered.

263. The first point which we may notice is, that chemical affinity, or capacity for combination, does not appear to exist between all substances. Thus, the elements fluorine and oxygen have never been made to combine, or found in combination; and the compounds of nitrogen and carbon with many of the metals are not known to exist. But it would be premature to say that they cannot exist. New methods of effecting combination are continually presenting themselves.

* We may, perhaps, conceive of a chemical compound as a sort of microcosm, a solar system in miniature, in which the particles of the different elements are in constant motion round each other, some being connected more intimately, like a planet with its satellites, forming a group or 'compound radicle,' as it is called, which is capable of being detached from the system as a whole.

264. In the next place, the mutual affinity of substances differs very greatly. One or two instances of this have been given already. We found that water was decomposed when treated with sodium, owing to the greater affinity of sodium for oxygen at ordinary temperatures, as compared with that of hydrogen. Again, iodine and phosphorus unite at ordinary temperatures; iodine and mercury do not combine until heat is applied.

265. It is not easy to say how much influence the state of the resulting compound—for example, its solubility, its tendency to become gas, &c.—has in determining a particular change. There is no doubt that the influence is sometimes very great. For example, when a solution of ammoniac carbonate is added to a solution of calcic chloride, a white precipitate of calcic carbonate is formed. We have here six substances: nitrogen, hydrogen, carbon, oxygen, calcium, and chlorine, brought into contact in presence of water. Of these, calcium, carbon, and oxygen can form a compound which is insoluble in water, and this compound is accordingly produced. But we should not be justified in inferring from this experiment that calcium had absolutely a stronger affinity for carbon and oxygen than ammonium (nitrogen and hydrogen) has. Much depends on the conditions of the experiment. Thus, if the mixture above mentioned is evaporated to dryness, and then further heated, a different change takes place: ammoniac carbonate is volatilised, and calcic chloride remains behind. The same substances are present, but the temperature is high. Now, ammonium, carbon, and oxygen can form a compound which is volatile at the temperature employed, and this is enough to determine the formation of that compound.

266. Another circumstance which modifies chemical combination is the condition of the substances taken. Solids very rarely act chemically upon each other; their particles do not admit of being brought into such close contact with each other as is required for chemical affinity to take effect. Again, when a substance is just being liberated from one combination, or in

the 'nascent state,' as it is termed, its affinity for other substances is often very greatly increased. Electrolysis affords some good examples of this. For instance, when a solution of argentic nitrate is electrolysed, the oxygen which is liberated at the positive pole unites with the adjacent particles of silver in the solution, and argentic dioxide is deposited in crystals. If a few drops of a solution containing arsenic are added to dilute hydric sulphate which is undergoing electrolysis, the hydrogen combines with the arsenic to form a gas, hydric arsenide. The hydrogen, instead of being liberated by the action of electricity, may be obtained by dropping a piece of zinc into the hydric sulphate to which the arsenic solution has been added; the one essential condition being that it must be liberated in contact with the substance on which it is to act. The probable explanation of this increased chemical activity of substances in the nascent state must be deferred until the atomic theory has been considered.

267. Let us now go on to examine one or two examples of chemical affinity, which have already been given in Chapter I., as instances of analysis and synthesis.

268. When the gases oxygen and hydrogen are mixed together they become uniformly diffused through each other, but no chemical combination occurs between them. If, however, a light be applied to the mouth of a vessel filled with the gases mixed in certain proportions; or, if an electric spark is sent through the mixture, a flash of light occurs, a sharp explosion is heard, and the gases become changed into steam, which, as it cools, condenses into water. The oxygen and hydrogen are now said to have entered into chemical combination, and to have formed water. The smallest conceivable quantity or molecule of water is supposed to consist of particles of hydrogen and oxygen, not fused or run into one larger particle, as two drops of a liquid metal like quicksilver flow into a bigger drop, but remaining as distinct and unlike particles kept near each other by a peculiar constraining force, to which the name has been given of chemical affinity. So long as

the particles of oxygen and hydrogen are under the influence of this power, they cease to present the properties which characterise oxygen and hydrogen when uncombined, the associated particles acting for the time as if they were but one, which manifests the properties peculiar to water. When water, again, is decomposed—for example, by a galvanic current—the particles of hydrogen separate from those of oxygen, and all those of one kind go together; the properties of water cease to appear; and those of hydrogen, on the one hand, and oxygen on the other, become manifest.

269. Again, to take the case of gunpowder, which is an intimate mixture of saltpetre, sulphur, and charcoal, formed by grinding the materials together for many hours. We are able, when a grain or two of it is broken up and placed under a powerful microscope, to distinguish the separate particles of saltpetre, sulphur, and charcoal. They lie there in juxtaposition, but not chemically combined. But when the temperature of the mixture is raised up to a certain point, the substances unite with a bright flash, and, if in a confined space, with explosion; and no vestige of the original ingredients remains, but, instead of them, we have a large volume of permanent gases, together with a small quantity of a gray solid, which constitutes the smoke.

270. It will be found, on a general review of the above and other chemical changes, that there are certain characteristics common to all of them.

271. (1.) *Heat is evolved during chemical combination.*—This is so universally true, that, in doubtful cases, the appearance of heat has been taken as decisive evidence that chemical combination has occurred. The union of oxygen and hydrogen, effected in the oxy-hydrogen blow-pipe, furnishes us with one of the most powerful sources of heat which we possess. The explosive force of gunpowder is mainly due to the enormous expansion of the gaseous products by the heat evolved during the chemical change.

272. (2.) *There is a change, more or less complete, of chemical and physical properties.*—A knowledge of the qualities of the

elements does not enable us to anticipate or predict what the properties of the compound will be, which we can, to a great extent, foresee in the case of mechanical combinations. Thus, the specific gravity of steam is not identical with that of either oxygen or hydrogen, or that of a mixture of them; nor is it the sum or the mean of the densities of those gases, taken singly or mingled. Its action on light, its conducting power for sound, its relation to combustion and to animal life, and a multitude of its other physical characters, are totally unlike those of a mechanical mixture of oxygen and hydrogen.

273. Of the changes in physical properties which chemical affinity produces, none is so likely to strike the beginner as the difference in colour between a chemical compound and its elements, or a mixture of these. Thus, if the pale yellow sulphur and the bluish-white quicksilver be heated together, they form the bright-red vermilion, a tint which cannot be produced by any mechanical mixture of blue, yellow, and white colours. In like manner, if a piece of the reddish-brown copper be dissolved in the colourless liquid nitric acid, it forms a deep-blue compound. When charcoal and sulphur unite, the resulting compound is neither black nor yellow, nor of any intermediate tint, but as colourless as water. Multitudes of other examples might be given, but these may suffice so far as change of colour is concerned.

274. The other properties of the chemical elements, however, are quite as much altered, when they combine, as their tints are. Thus, the heavy metal antimony, which we are accustomed to see as a massive solid, forms an invisible gas when it combines with hydrogen. The greenish-yellow gas chlorine, on the other hand, when it unites with quicksilver, forms white crystals of corrosive sublimate. Solid sulphur and charcoal change into a very volatile liquid. Phosphorus, which resembles wax in appearance, and oxygen, a colourless, invisible gas, form phosphoric pentoxide, a body exceedingly like snow. Charcoal, hydrogen, and oxygen are all tasteless; gum is one combination of them, arrow-root another, sugar a third.

275. Chlorine gas has a suffocating odour; common salt, of which it forms more than one half by weight, is odourless. Charcoal and hydrogen, on the other hand, have no odour; nevertheless, a large number of our choicest perfumes, such as attar of roses, oil of bergamot, and oil of citron, consist solely of those two elements. In like manner, the scentless nitrogen and hydrogen are the only constituents of one of the most odorous of all substances, spirits of hartshorn, or ammonia.

276. Again, the deadly poison prussic acid is made up of carbon, hydrogen, and nitrogen, which, taken singly or mixed, are not directly injurious to animal life. Oxalic acid, another poison, consists of charcoal, hydrogen, and oxygen. The same elements constitute spirits of wine and sulphuric ether.

277. The preceding examples of change in specific gravity, colour, form, taste, odour, and relation to living animals, will serve, in the meanwhile, to prove how totally dissimilar in properties a chemical compound is from a mere mechanical mixture of its elements.

278. (3.) *A chemical compound cannot be broken up by simple mechanical means, such as solution or diffusion.*—When a mixture of oxygen and hydrogen is placed in a jar standing over mercury, the upper end of the jar being closed by a plate of porous earthenware, and the whole being placed under the receiver of an air-pump, the hydrogen passes out, or diffuses, through the porous plate four times as quickly as the oxygen, so that, in a short time, the mixture in the jar will no longer explode on the application of a light. Steam will also pass through a porous plate; but that which passes through, as well as that which remains, is still steam, unaltered in composition.

279. Again, of the three constituents of gunpowder, saltpetre is the only one which is soluble in water. If, then, some gunpowder is placed in a flask, and boiled with about four or five times its weight of water for a short time, the mechanical mixture is broken up. The saltpetre enters into solution in the water, and, when the whole is poured upon a strainer, or

'filter,' as it is called, of porous blotting-paper, placed in a funnel (fig. 25), all the charcoal and sulphur remain mixed on the filter, while the liquid which passes through is a solution of saltpetre, and will deposit crystals of the salt on cooling. If some more water is poured upon the mass in the filter, and this process of washing repeated two or three times, the whole of the saltpetre will be separated, and may be recovered unaltered in properties, by evaporating the solution, that is, by heating it in a basin over a lamp until all the water is driven off.

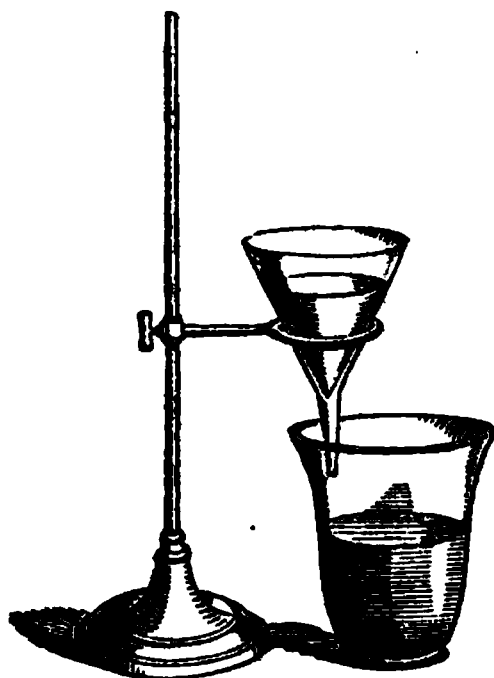


Fig. 25.

280. Similarly, to separate the sulphur and charcoal, we may take a liquid which dissolves the former, and not the latter. Such a liquid is carbonic disulphide (itself, it may be remarked, composed of the very same substances which it is used to separate); and if the residue of sulphur and charcoal, after having been dried, is warmed for some time with this liquid,* the sulphur dissolves, and may be separated by filtration, as described above, the charcoal remaining on the filter. If a little of the yellowish filtrate is placed in a watch-glass, it will very shortly deposit crystals of sulphur as the disulphide evaporates.

281. If we collect the products of the explosion of gun-powder, we find ourselves unable to obtain the saltpetre, sulphur, and charcoal by the above means. An entire rearrangement of particles has taken place, and we obtain indeed a mechanical mixture (consisting chiefly of carbonic dioxide, steam, nitrogen, and potassic sulphide), but one which requires an entirely different set of solvents to separate its constituents.

* The flask containing the mixture should be placed in a basin of warm water, and no lighted lamp should be near, on account of the ready volatility and inflammability of the disulphide.

282. (4.) *No weight is lost in chemical combination.*—This may be illustrated by the following experiment. A strong tube, about 1 cm. in diameter and 20 cm. in length, is sealed at one end, and 2 grms. of mercury and 2.5 grms. of iodine are introduced into it. The open end is then drawn out and sealed hermetically, especial care being taken to make both ends thick and strong, and to anneal the glass thoroughly, as it has to stand some pressure. The tube with its contents is next weighed, and chemical combination between the mercury and iodine is caused to take place by heating the tube gently over a lamp. The resulting compound, mercuric iodide, will at first be liquefied by the heat evolved, but when cool will be seen to be a scarlet solid. If the tube is now again placed in the balance, no loss or gain of weight will be perceptible.

283. (5.) *Chemical combination takes place only in certain definite proportions by weight.*—A mechanical mixture may contain its ingredients in any proportion whatever. Glycerine and water, for instance, may be mixed in any quantities, and may be separated by the mechanical process of distillation. Two measures (or 32 parts by weight) of oxygen will form a mechanical mixture with two measures (or 2 parts by weight) of hydrogen; but if we try to effect chemical combination by the electric spark or otherwise, we find that the gases do not wholly disappear, but that one measure of permanent gas remains uncombined, which may be proved to be oxygen. The same is observed if, say, three measures of hydrogen are taken with one measure of oxygen. The gases, in a word, refuse to combine in any other proportion than that of 2 : 1 by volume, or 2 : 16 by weight. So also in the experiment given in par. 282, if more than 2 grms. of mercury are taken for every 2.5 grms. of iodine, some of it will remain unaltered after heat has been applied; a compound, consisting of 200 parts of mercury united with 254 parts of iodine, being the only one which it is possible to form under the conditions of the experiment. This subject of combination by weight is of such fundamental importance, that it will be discussed more fully in the next chapter.

CHAPTER IX.

LAWS OF COMBINING PROPORTION.

284. The laws of chemical combining proportion are four in number. They refer to combination by *weight*, not to combination by volume, which will be referred to in another portion of the work. They explain certain exceedingly simple principles which regulate the relative quantities or proportions by weight, according to which chemical substances unite with each other to form combinations. A knowledge of them is essential to the successful prosecution of chemistry, whether as a science or an art. It is of the utmost importance, therefore, that the student should clearly comprehend them.

285. The first is best entitled THE LAW OF CONSTANT PROPORTION. It teaches that

THE SAME SUBSTANCE ALWAYS CONSISTS OF THE SAME ELEMENTS UNITED IN THE SAME PROPORTION.

Water not only consists invariably of oxygen and hydrogen, but the weight of oxygen present is always eight times greater than that of hydrogen. Common salt always contains $35\frac{1}{2}$ parts of chlorine to 23 of sodium; vermilion, 32 of sulphur to 200 of mercury; so also marble has always 40 parts of calcium united with 12 of carbon and 48 of oxygen; sal ammoniac, $36\frac{1}{2}$ of muriatic acid to 17 of ammonia.

286. It is important to observe how much chemistry is simplified by the existence of such a law as we have just explained. A single accurate analysis not only settles once for all what the ingredients of a compound are, but also what the

proportion of these ingredients is. It is true that in actual practice the chemist never contents himself with a single analysis, but he does this, not because he expects one specimen, for example, of water, to differ in composition from another, but because his methods of analysis, however refined, still fall far short of absolute accuracy. It is essential, accordingly, to make several analyses which yield results differing very slightly from each other, and the mean or average of those several determinations is taken as representing the true composition of the body. After all, however, the several imperfect analyses are only equal to a single accurate one.

287. In the case of mechanical mixtures, on the other hand, or of combinations, consisting partly of definite chemical compounds, and partly of indefinite mixtures, the labours of the chemist are enormously greater, and one analysis applies only to the particular specimen upon which it is made. Thus clay, mortar, garden earth, or soil, many dyes, perfumes, and medical preparations, &c., are not constant chemical compounds. To determine the composition of a single specimen would require, as in the case of a chemical compound, several analyses, the mean of all of which should afterwards be taken. But the very next parcel of the substances named, which called for a knowledge of its composition, would require an analysis to be made as carefully as if no other specimens of those bodies had been previously examined. It is otherwise with chemical compounds. The composition of one specimen of water is the composition of all specimens of water, whether derived from melted snow or from springs, or formed by chemical combination in the laboratory. The marble of Italy is identical with the marble of Ireland. The vermilion made in China is identical with that made in England.

288. The service which a knowledge of this law renders to chemistry as a practical art is not less striking. In the preparation of dyes, pigments, medicines, metallic alloys, such as brass, and important chemical compounds, such as glass, soap, carbonate of soda, and the like, the chemical manufacturer can

avoid all useless waste of material on the one hand, and all unwise economy of it on the other. There is one proportion, and one only, in which the ingredients of the substance he is manufacturing require to be supplied. The employment of more than that proportion is a waste of material; the employment of less is a detrimental withholding of it.

289. The second law of combining proportion is related to the circumstance, that the same elements in almost every case combine in more than one proportion to constitute several compounds. If this, in truth, were not the fact, we should never succeed, even with sixty elements at our disposal, in accounting for the enormous variety of substances found in our globe. This law is named that of MULTIPLE PROPORTION, and enforces the truth that,

WHEN ONE BODY COMBINES WITH ANOTHER IN SEVERAL PROPORTIONS, THE HIGHER PROPORTIONS ARE MULTIPLES OF THE FIRST OR LOWEST.

Thus, oxygen and hydrogen are contained in water in the ratio of 16 parts of the former to 2 of the latter. Those elements, however, unite to form a second compound, named the hydric peroxide, or oxygenated water, in which the oxygen is to the hydrogen in the proportion of 32 to 2; or, the hydrogen remaining the same as in water, there is exactly *twice* as much oxygen. The illuminating power of coal-gas is owing to the presence in it of two substances, each a compound of carbon and hydrogen. In the one (olefiant gas) there are 12 parts by weight of carbon to 2 of hydrogen. In the other (fire-damp), 12 of carbon to 4 of hydrogen; or, the weight of carbon being the same in both, there is exactly twice as much hydrogen in the second as in the first.

290. If we now write down in a row the compounds we have named, the multiple relation will be more clearly perceived:

| | | |
|----------------------|---------------|-------------------------|
| Water..... | = Hydrogen 2, | Oxygen 16. |
| Hydric Peroxide..... | = Hydrogen 2, | Oxygen 32, or twice 16. |
| Olefiant Gas..... | = Carbon 12, | Hydrogen 2. |
| Fire-damp..... | = Carbon 12, | Hydrogen 4, or twice 2. |

291. One of the most remarkable examples of this law occurs in the compounds of nitrogen and oxygen, which are five in number. The proportion of nitrogen is the same in all, and may be represented by the number 28, while that of the oxygen, which, in the lowest, may be expressed by 16; in the second, is 32, or twice 16; in the third, 48, or three times 16; in the fourth, 64, or four times 16; and in the fifth, 80, or five times 16. The higher proportions are thus multiples of the lowest by 2, 3, 4, 5, at which last number, in this case, they stop. This will appear more distinctly by the following table, containing the names of the five compounds of nitrogen and oxygen:

| | | |
|------------------------|--------------|---------------------|
| Nitrous Oxide..... | Nitrogen 28, | Oxygen 16. |
| Nitric Oxide..... | Nitrogen 28, | Oxygen 32 = 16 × 2 |
| Nitrous Anhydride..... | Nitrogen 28, | Oxygen 48 = 16 × 3 |
| Nitric Peroxide..... | Nitrogen 28, | Oxygen 64 = 16 × 4 |
| Nitric Anhydride..... | Nitrogen 28, | Oxygen 80 = 16 × 5. |

292. In every series of compounds we find the same law operating. If a substance can combine with more than 16 parts of oxygen, the least next quantity it combines with is 32. It never combines with $16\frac{2}{3}$, $16\frac{4}{5}$, $16\frac{9}{10}$, or any other fraction whatever; but if it overstep the 16, goes right on to the 32 before it is again saturated. It may go past the 32, but in that case it cannot stop at any intermediate number short of 48. It need not halt at 48, however, if it can go on to 64; or at 64, if it can combine with 80; and it may pass at once from 16 to 80, or to any other quantity, however large, provided it be a multiple of the original 16. The only unalterable decree is, that whatsoever smallest quantity of one body another can combine with, every higher compound must contain in increasing multiples.

293. The law of multiple proportion furnishes a great help to the memory in recollecting the composition of complex compounds. Analysis only can tell us exactly how much of any ingredient is present in a compound; but of this we are certain before, and indeed without analysis, that each

constituent will be present either in its smallest combining quantity, or in a multiple of that. The amount of oxygen in all its compounds may be expressed by 16, or a multiple of 16. All combinations of sulphur contain either 32 parts of it, or if not, then 64, 96, or some other multiple of 32. Iron occurs in quantities of 56, 112, &c.—that is, its quantity, if above 56 parts, can always be expressed by a number divisible by 56 without a remainder.

294. The third law of chemical combination is called THE LAW OF RECIPROCAL PROPORTION. It states that

IF TWO BODIES COMBINE WITH A THIRD, THE PROPORTIONS IN WHICH THEY COMBINE WITH THAT THIRD BODY ARE MEASURES OR MULTIPLES OF THE PROPORTIONS IN WHICH THEY MAY COMBINE WITH EACH OTHER.

For instance, carbon unites with oxygen in the proportion of 12 parts by weight of carbon to 16 parts of oxygen. Hydrogen unites with oxygen in the proportion of 2 parts to 16 parts. We know of a compound of carbon and hydrogen—namely, marsh gas, or fire-damp—in which 12 parts of carbon are united with 4 (or 2×2) parts of hydrogen. Again, nitrogen unites with oxygen in the proportion of 28 parts to 16 parts. We should, if the law is correct, expect to find a compound of nitrogen and hydrogen in the proportion of 28 to 2, or a measure or multiple of these numbers. Now, ammonia is found to contain 28 parts of nitrogen united with 6 (or 3×2) parts of hydrogen.

295. The fourth and last law which we have to consider is a very simple one, and will not require much illustration. It may be called THE LAW OF COMPOUND PROPORTION, and states that

THE COMBINING PROPORTION OF A COMPOUND IS THE SUM OF THE COMBINING PROPORTIONS OF ITS CONSTITUENTS.

This follows as a natural consequence of the other laws in connection with the fact that no weight is lost in combination. As an example, we may take the following: Sulphuric trioxide

consists of sulphur and oxygen united in the proportions of 32 to 48. The sum of these two numbers is 80. Water consists of hydrogen and oxygen in the proportions of 16 to 2. The sum of these numbers is 18. Now, when sulphuric trioxide unites with water, it does so in the proportion of 80 parts of the trioxide to 18 parts of water. We know, moreover, of a great number of crystallised salts, such as blue vitriol, or cupric sulphate, and Epsom salts, or magnesian sulphate, containing a certain amount of water which appears essential to their crystalline form; but in no case can we consistently represent the proportion of water associated with the salt by any other number than 18, or a multiple of 18.

296. In virtue of these laws, a number can be found for every body, simple or compound, expressing the ratio in which it combines with others. Such numbers are derived from the results of experiments, and are quite independent of any theory as to the constitution of matter. Any series of numbers may be taken, provided only that the proper proportion is maintained among them. Thus, analysis demonstrates that the combining quantity of oxygen is 16 times greater than that of hydrogen; so also it shews that the combining quantity of charcoal or carbon is 12 times greater than that of hydrogen; that of nitrogen, 14 times; that of sulphur, 32 times; that of iron, 56 times. Now any scale of numbers may be taken to represent these relative combining quantities, provided only that the number for carbon be 12 times greater than that for hydrogen; that for oxygen, 16 times greater; that for nitrogen, 14 times; that for sulphur, 32 times; and that for iron, 56. Thus we might call iron 1; nitrogen would then be $\frac{1}{4}$, or 0.25; and hydrogen would be $\frac{1}{56}$. Or oxygen might be made 1, in which case hydrogen would have its combining quantity expressed by $\frac{1}{16}$, and sulphur by 2. We may give any value we please to any one of the elementary bodies we choose to fix upon for a commencement, and call it 1, 10, 100, 1000, $\frac{1}{2}$, $\frac{1}{4}$, or any other integer or fraction; but here our liberty ceases. The relations between the numbers are absolute, though their individual

value is not; and from the settled figure we must count upwards or downwards, or both ways, so as to maintain inviolate the relative values throughout the series.

297. Different scales of combining numbers, accordingly, are in use among chemists. Thus, for analytical purposes it is preferable to call oxygen 100; but in teaching, it is found much more convenient to begin with hydrogen, and to call it 1, so that we count only upwards. The numbers in this scale are all small, and do not, in the majority of cases, go beyond two integers. A few examples of the combining weights of some of the elementary bodies on both the hydrogen and oxygen scales are given below:

| Name of Element. | Hydrogen Scale. Hydrogen equal to 1. | Oxygen Scale. Oxygen equal to 100. |
|------------------|---|---------------------------------------|
| Carbon..... | 12 | 75 |
| Nitrogen..... | 14 | 87.5 |
| Sulphur..... | 32 | 200 |
| Iron..... | 56 | 350 |
| Hydrogen..... | 1 | 6.25 |
| Oxygen..... | 16 | 100 |

298. These numbers follow exactly the same proportion; 6.25 bears the same relation to 75 that 1 does to 12; 87.5, the number for nitrogen, is exactly 14 times greater than 6.25, the number for hydrogen. The same numerical relation, accordingly, is expressed by both scales. We shall always employ the hydrogen series, as giving small numbers easily apprehended and remembered, and a complete table of combining numbers will be found on p. 136.

* * The laws of combining proportion, and the atomic theory which occupies the next chapter, cannot be profitably studied by those who are entirely unacquainted with the names and properties of chemical substances. It is advisable, therefore, to postpone the study of the laws and theory till the properties of at least oxygen, hydrogen, and nitrogen, as discussed under these titles, have been explained and illustrated. The student will then be familiar with a sufficient number of examples of combinations in different proportions, to follow, without difficulty, the exposition contained in this chapter; nor is it desirable to adjourn its discussion to any later period than the earliest at which it can be intelligently followed.

CHAPTER X

ATOMIC THEORY.

299. The laws of combining proportion, which have been explained, are not doubtful theories or hypothetical speculations. They are the expression or statement of facts, ascertained by direct and multiplied observation; and any one who questions their truth, can satisfy himself of their reality by accurately analysing a few chemical compounds.

300. These laws, however, were first made known to chemists by their chief discoverer, Dalton, in connection with a peculiar hypothesis, or, as it is less properly but more commonly called, theory, which supplied a beautiful and complete explanation of the existence of such laws, and furnished at the same time a very simple and easily followed mode of teaching them. It was with great ingenuity and boldness conjectured by this chemist, that the elementary bodies were composed of extremely small indivisible particles, which he called *atoms* (from the Greek word *ἄτομος*—that which cannot be divided), and that these atoms differed in weight. This difference in weight he considered to account for the different combining proportions of the elements, all compounds being formed by the union of atom with atom.

301. As oxygen, for example, has a combining proportion 16 times greater than that of hydrogen, so the ultimate atom of oxygen is assumed to be 16 times heavier than the ultimate atom of hydrogen. As the combining proportion of nitrogen is

14 times that of hydrogen, so the atom of nitrogen is supposed to be 14 times heavier than that of hydrogen: and in like manner the relative weights of the atoms of the other elementary bodies are supposed to differ by the same numbers that the relative weights of their combining proportions differ by. Dalton, it will be observed, thought that if it were possible by any means to select single atoms of each of the elementary bodies, and weigh them one by one, we should find, *first*, that different atoms of the same element possessed all the same weight, so that whatever was the absolute weight of any one, would be found to be the weight of each of the others of the same kind; and if one atom of hydrogen weighed the millionth of a millionth of a gramme, each of the hydrogen atoms would weigh the millionth of a millionth also; *secondly*, we should find that all the oxygen atoms were 16 times heavier than the hydrogen ones; all the nitrogen atoms, 14 times heavier; all the silver atoms, 108 times; all the gold atoms, 197 times heavier. In short, the proportions in which bodies combine with each other are supposed to depend upon the weights of the atoms which make them up, and to be identical with these weights. All the numbers, accordingly, which, before this hypothesis is considered, represent combining proportions, as soon as it is adopted, come to represent weights of ultimate atoms, or atomic weights.

302. It may seem singular that it should be considered important to explain Dalton's atomic views, seeing that it is not at all certain that there are such things as atoms, much less that they differ in relative weight.

303. The conception, nevertheless, of the combining proportion of each element, as dependent on the special and constant weight of the ultimate particles of which masses of the element consist, greatly facilitates the apprehension and remembrance of the laws of combining proportion. Whether an atom is absolutely indivisible, is not a question which chemistry requires to decide. It is enough for the solution of the problems of the science, if we concede that in fact those atoms do not suffer

division; in other words, are not lessened in weight when chemical combination or decomposition occurs. It is much less easy to grasp the idea of a constant numerical ratio, or combining proportion, than it is to conceive of a solid, ponderable mass, which is as unchangeable in relation to gravity as the weights of a balance. Nor is the value of this latter conception in simplifying the study of chemistry, affected by the fact, that the solid, ponderable masses referred to may admit of reduction in size, and therefore in weight, by forces other than chemical.

304. A homely comparison may assist in making this clear. Many of our rare or valuable articles of commerce are offered for sale in fixed quantities, so that the purchaser must either take a certain amount at a time, or obtain none. Thus, attar of roses is brought to this country in small stoppered phials, which the dealer will not open so as to dispose of less than the whole contents of the phial at a time. Still more familiar examples are afforded by the dealers in the more valuable teas, who sell these only in packages of a fixed weight; for example, a pound. Weighed quantities of arrow-root, in like manner, are offered for sale in boxes, which the seller will not open. We may liken the different elementary bodies to substances sold in this way. Each of them may be regarded as furnished by nature, made up into small parcels or quantities having a fixed weight, which is the same for each parcel of the same element. Hydrogen can be obtained in quantities smaller than any of the other elementary bodies. Each little parcel of carbon is 12 times heavier than each little parcel of hydrogen. Nitrogen is supplied in quantities 14 times, and iron in quantities 56 times, greater than hydrogen. None of these bodies is found occurring in nature otherwise than parcelled out in the way we have supposed, and none of them is made up into larger parcels or made down into smaller ones during any chemical change. This is all the atomic theory need be considered as contending for.

305. The beginner, then, adopting this view, may at once exchange for the abstract and shadowy conception of numerical

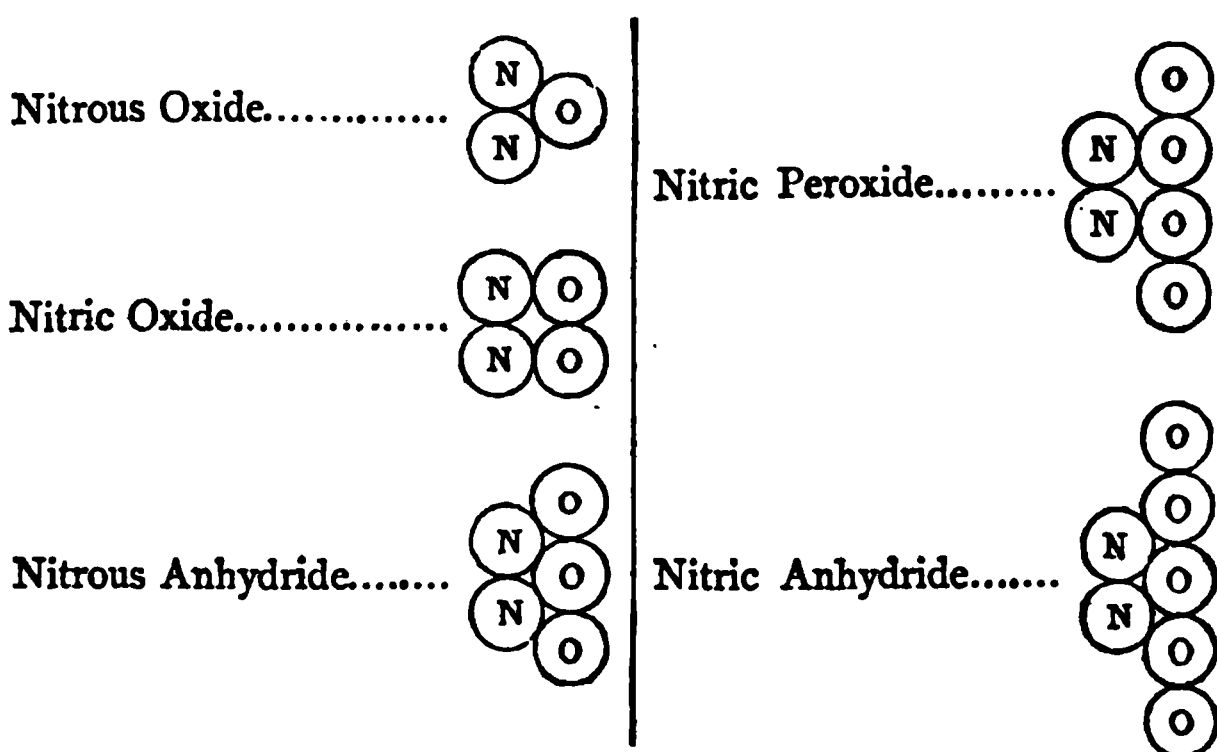
ratio, or combining proportion, the distinct and easily apprehended idea of a solid ponderable atom. 1 is to be considered as stamped upon every particle of hydrogen, as if the whole amount of it in the globe had been coined at the same mint into pieces of exactly the same value. Carbon, in like manner, has its atoms stamped with 12 upon them, sulphur with 32, iron with 56.

306. When the elementary bodies, moreover, enter into combination, their atoms, bearing the unalterable stamp upon them, follow, of necessity, laws such as we have discussed in the preceding section. Thus, if every atom of oxygen is 16 times heavier than every atom of hydrogen, then different specimens of water must be identical in composition. Eighteen grammes of it will, on analysis, yield 16 grammes of oxygen, and 2 grammes of hydrogen; 18 kilogrammes, in exactly the same way will afford 16 kilogrammes of the one element, and 2 of the other, because, the constituents of water existing in it in the proportion of 1 atom of the one to 2 atoms of the other, and the atom being unalterable in weight, every specimen of water must yield exactly half the number of atoms of oxygen weighing 16 as of hydrogen weighing 1, so that it will be found to contain a ninth of its weight of one gas, and eight-ninths of the other. The law of *constant* proportion, then, is easily accounted for.

307. The law of *multiple* proportion is equally necessary, for an atom of one element is the smallest quantity that can be added to a compound containing an atom of it already, and whatever was the weight of the first atom will be that of the second also, so that an exact duplication of the first proportion, without any fractional lack or excess, must take place. And if more than one atom be added at a time, it must be atoms, not an atom and a half, or one and a third, or any other fraction or fragment; for this cannot be, seeing that the atom is chemically indivisible.

308. In the five compounds of nitrogen and oxygen already considered, the first, which contained 28 parts by weight of the

former to 16 of the latter, is believed, on very strong grounds, to be a combination of 2 atoms of nitrogen with 1 of oxygen. The next, which contains more oxygen, cannot contain less than two atoms of it, and the proportion of oxygen will therefore be twice 16, or 32; the third will contain three atoms, corresponding to a proportional weight of 48; and so on with the rest. The following diagram will illustrate this. Each atom is represented by a circle with the initial letter, representing the name of the element of which it is an ultimate particle:



309. The law of reciprocal proportion is an equally inevitable result of the atomic nature of chemical combination. For an atom will exhibit the same proportional weight, whatever be the body with which it combines: and when we have once determined the weight of an atom by the examination of any compound, we may feel sure that, if the determination is a correct one, that weight, or a multiple of that weight, will be found in every other compound containing the element in question.

310. Lastly, the law of *compound* proportion could not fail to manifest itself according to the atomic theory; for the aggregation of atoms does not alter their weight, and the atom is not divisible by the forces which effect chemical analysis, so that its weight should be shared among smaller molecules. Had

the atom been divisible, it might have been otherwise; and when two or more atoms entered into combination, they might have broken up into lesser particles, among which the original weight was parcelled out.

311. According to the atomic theory, however, the atom is chemically indivisible; the combining proportion, therefore, or weight of the molecule of water, for example, is necessarily 18, because it consists of three atoms weighing respectively 16, 1, and 1. The weight of the molecule of water is as necessarily 18 as the value of a penny and a sixpenny-piece, taken together, is sevenpence.

312. In speaking of the ultimate particles of matter, use has been made of both the terms 'molecule' and 'atom.' It is highly important to bear in mind the conventional distinction between them, and the following considerations may serve to make it clear.

313. We are able, by mechanical means, such as pulverisation, to carry the subdivision of bodies very far. Thus, a lump of marble may be reduced in a mortar to a powder which is impalpable—that is, of which the particles cannot be separately appreciated by the sense of touch. But, if we place some of this powder under a powerful microscope, we can readily see that each particle of it has a sensible size, and might conceivably be divided into smaller particles. Again, a drop of water may be subdivided into smaller drops, such as we see in clouds or mist. But even these are comparatively large portions of water. When we raise water into steam, its particles in that condition are so small that they practically cease to reflect light, and are invisible under the highest magnifying power we can command. According to the atomic theory, this subdivision cannot be carried on indefinitely far, and we should at last reach a point beyond which we could only subdivide a particle of water into its elements, oxygen and hydrogen, and not into smaller particles of water. Such an ultimate particle of water is called a *molecule*, and it is best defined as '*the smallest quantity of a substance which can exist in the free state.*'

314. But this molecule, as we have seen, is of compound structure. We can, by various means, break it up into particles of oxygen and hydrogen. At this point our power of subdivision, according to the theory, ceases; and we call each of these ultimate particles of elementary substances *atoms*. The atom may therefore be defined to be '*the smallest quantity of an element which can enter into chemical combination.*'

315. It was formerly thought that the molecule of an element was the same as its atom; but there are strong reasons for believing that, with a few exceptions, this is not the case, but that the molecule is composed of two or more similar atoms chemically combined. The molecule of the gas hydrogen, for instance, is composed of two atoms of the element hydrogen, united together, and behaving, so far as physical experiments go, like one particle. If this is true, it follows that we have never yet isolated and examined the properties of the elementary body we call hydrogen. We can transfer it from one compound to another, but we cannot arrest it in its passage. It is a strong proof of the correctness of the above view that, in many cases, we find new or intensified properties manifesting themselves at the moment of the transfer, or when the body is in the 'nascent state,' which has been before alluded to; when, in fact, it has been eliminated from one molecule, and has not yet satisfied its combining affinities by forming another molecule.

316. Another argument is that, in some cases, we appear to be able actually to form a molecule of an elementary body by the synthesis of two atoms from different sources. Thus, when hydric peroxide is added to argentic oxide suspended in water, an effervescence takes place, and oxygen is evolved. We find, on examination, that both bodies are decomposed, and lose oxygen in exactly equal proportions, water and metallic silver being the results. The natural interpretation of this is, that an oxygen atom from the hydric peroxide has combined with an oxygen atom from the argentic oxide, to form a molecule of the gas oxygen.

317. It will be desirable also to give an explanation here of

the term 'radicle,' although it is really independent of the atomic theory. It is derived from the Latin word *radicula*, a small root, and means primarily any substance which is the basis or common ingredient of a series of compounds. Radicles are divided into two great classes, namely :

(A.) *Simple radicles*, which include all the elements. Thus, sodium is the radicle of a series of compounds, in which it is combined with oxygen, sulphur, chlorine, &c.

(B.) *Compound radicles*, of which cyanogen and ammonium are examples, and which consist of two or more elements united so closely as to behave in many chemical reactions like a single body. Thus, cyanogen, which is composed of carbon and nitrogen in the proportion of 12 parts of carbon to 14 parts of nitrogen, is the basis, or radicle, of a series of compounds which much resemble those of chlorine. We can transfer this compound substance from one combination to another, just as we can transfer chlorine. In the same way, a compound of 4 parts of hydrogen with 14 parts of nitrogen constitutes the radicle *ammonium*, which behaves in many ways like the element sodium, combining, like the latter, with chlorine, sulphur, cyanogen, &c.

318. In order that a body should be recognised as a radicle, it is not necessary that it should have been isolated. We have never succeeded in isolating fluorine, and yet we have no hesitation in speaking of it as an element. So, although we have never obtained ammonium in a separate form, yet, from the examination of a large number of compounds which agree only in containing 14 parts of nitrogen and 4 of hydrogen, we speak of these elements in these proportions (or, according to the atomic theory, of this group of atoms), as though they constituted an existing, isolable substance. Radicles correspond, in fact, exactly to the factors which make up an algebraic formula.

. A series of coloured balls, with a different colour for each of the chief elements, will be found of service in illustrating the atomic theory. A white

ball, for example, may represent an atom of oxygen, and a black ball one of hydrogen ; whilst one white ball and two black balls placed together represent a molecule of water. A better device, however, is a set of cubes of wood, with the initial letters or symbols of the elements marked upon them. If the cubes are stained black, they may be lettered with chalk, and eight or twelve will be sufficient. They have the advantage over balls of standing securely, and admitting of being placed close together in vertical or horizontal rows. The letters also upon them are much more significant than colours, and they may be employed with great advantage to illustrate the nature and steps of all the chemical reactions which are discussed throughout this work. Each cube will admit of six *symbols*, or initial letters, being marked upon it, one on each face ; but it is not advisable to letter more than one face of each cube.

CHAPTER XI.

CHEMICAL NOMENCLATURE.

319. The names or appellations by which the chemist distinguishes the various simple and compound substances are as much as possible constructed on a system, so as to supply information concerning the properties of the body; and if it be a compound, to tell the nature, and also the proportion, of its elements.

320. The nomenclature of chemistry is in this respect much superior to that of many of the other sciences, which give to everything they have to name a quite arbitrary title, so that the learner has first to make an effort of the memory to retain the term, and next, by a separate endeavour, to recollect what it denotes. Thus in mineralogy many substances are named in honour of individuals; and we read, accordingly, of Greenockite, Dolomite, Thomsonite, &c.—terms which give no information whatever concerning the nature and properties of the mineral.

321. Chemical nomenclature, notwithstanding, is defective, and will long remain so. Only a perfect knowledge of chemistry could secure a perfect nomenclature. In the meanwhile, our knowledge has outrun our skill in devising names, the system on which we set out at the beginning of this century having proved not nearly expansive enough to supply appellations for the multitude of unexpected new substances which

have recently been discovered. It would be unwise, however, till we are acquainted with a much greater number of compounds than we yet know, to make a fundamental change in chemical nomenclature.

322. The rare and valuable metals, having attracted the attention of mankind from the remotest historical periods, have received names which are still to a great extent retained. The combustible constituent of oil of vitriol has the two names brimstone and sulphur. Most of the familiar salts have more than one title, as potassic nitrate is called also nitre and saltpetre; cupric sulphate, bluestone and blue vitriol; ferric sulphate, copperas and green vitriol.

323. A few names have come down to us from the languages of the civilised nations of antiquity. The root, for example, of the word ammonia (spirits of hartshorn) is some thousand years old—Ammon, from which it is derived, having been the name of one of the gods worshipped by the ancient Egyptians, from whom the Romans transmitted the name to us.

324. In the ninth century the Arabians were the most distinguished chemists, and several of the names they introduced still survive. Many of them may be recognised by commencing with the Arabic definite article *al*. Thus we have alcohol, alkali, alembic.

325. During the fifteenth and sixteenth centuries, the European alchemists were the most famous students of chemistry. We still retain many of their quaint, fanciful, but often expressive names—such as spirit of wine, spirit of hartshorn, spirit of salt, flowers of sulphur, aqua regia.

326. Astrology and alchemy went hand in hand, nor have we yet ceased to use some of the terms introduced by the astrological chemists. Nitrate of silver still bears the name of lunar caustic, and crystallisations of silver are called the tree of Diana: silver and the moon (Luna or Diana) having been astrologically connected. In like manner, in unscientific works, one of the compounds of iron is still styled crocus Martis, in reference to the planet Mars, with which iron was associated.

The metal quicksilver is not likely soon to lose its astrological name of Mercury.

327. In the seventeenth century, the adoption of an erroneous theory of combustion led to the adoption of a nomenclature now totally abandoned. As none of its terms occur systematically in works of the present day, we say no more concerning it. Those, however, who wish to read works on chemistry published in the last century, many of which are of the greatest interest and importance, must make themselves acquainted with this nomenclature, which continued to be employed till the very close of the eighteenth century.

328. At that period the recognition of another theory of combustion, the discovery of many new gases, the detection of the composition of the air, and of that of water, revolutionised all chemistry, and led to the introduction of a nomenclature which has lasted until quite recent times.

329. The names of the elements we have given already. They are entirely arbitrary, and many of them were words of common language before they were adopted as scientific terms. In the case of the elements more recently discovered, an endeavour has been made to give names of similar termination to those which resemble each other. Thus all the metals discovered within this century have their names terminated in *um*, as potassium, sodium, lanthanum; and the names of all the metals terminate similarly, if their Latin appellations be used.* Thus lead in Latin is *plumbum*; copper, *cuprum*; antimony, *stibium*, &c. With two exceptions, moreover (selenium and tellurium), no element which is not a metal has its name terminated in *-um*.

330. It is of importance to the student to remember this, and to notice that the table of elementary bodies is a list rather of Latin than of English names. The proof of this will be given in the next chapter.

331. Three of the elements, resembling each other in

* Except mercury, the Latin name for which is *hydrargyrus*.

properties, and in several respects unlike the others, have their names ending in *-on*—namely, carbon, boron, silicon. The names of another remarkable group of elements end in *-ine*—chlorine, bromine, iodine, and fluorine.

332. Many organic radicles have names assigned to them which end in *-yl* (from the Greek *ὑλη*, matter, basis), and this termination is becoming a common one for inorganic radicles also. Thus we have methyl, ethyl, &c. for the hydrocarbon radicles of the alcohols, and sulphuryl, carbonyl, nitryl, and others, in inorganic chemistry.

333. No community of property is intended to be represented by the termination in *-gen*, common to oxygen, hydrogen, and nitrogen. Sulphur and phosphorus had received names long before our present system of nomenclature was devised; but these being distinctive and euphonious, and readily permitting adjectives to be derived from them, were willingly retained. The titles of the elements will be further considered in treating of each.

334. There are at present, unfortunately, several systems of nomenclature in use in this country. Almost every writer has considered it expedient to introduce modifications of his own, and it is not easy to see where a sufficient authority exists to settle the question, and decide between the different systems. The student must therefore be prepared to hear the same thing called by different names according to the place where he happens to be working.

335. The modern systems agree in being based on the conception of radicles explained in the last chapter. Names are given to the various radicles, which are intended to express, more or less completely, their composition and character. These names differ in mode of formation according to the electric relation (so far as it can be ascertained) in which the radicles stand to each other in the compound.

336. (1.) As regards the more electro-negative radicles. The terminations of their ordinary names are altered into *-ide*, *-ite*, or *-ate*; the two latter terminations denoting that oxygen is

considered to be present in the radicle.* The termination *-ate* implies a radicle which contains more oxygen than that which has the termination *-ite* assigned to it.

337. Thus, salts containing the chlorine radicle are called chlorides; compounds containing a radicle in which chlorine is associated with oxygen are called chlorites or chlorates, according to the amount of oxygen they contain; compounds containing the sulphur radicle are called sulphides, those containing the oxygen radicle are called oxides.

338. Some few substances, such as chlorine and sulphur, form, in association with oxygen, more than two radicles. In these cases, the terminations *-ite* and *-ate* are retained unaltered and without addition for the central members of the series, while the higher and lower radicles are distinguished by the prefixes *per-* (*hyper-*) and *hypo-* respectively. Thus the radicles containing chlorine and oxygen are named, starting from that which contains least oxygen, hypochlorite, chlorite, chlorate, perchlorate.

339. When there is more than one atom† of a radicle present in the compound, the number of atoms is, by most chemists, expressed by the addition of a prefix derived from a Greek numeral,‡ *di-*, *tri-*, *tetra-*, *penta-*, &c. Thus a series of oxides is often written as monoxide, dioxide, trioxide, tetroxide, pentoxide, &c. Sometimes the prefixes *proto-* and *per-* are used as expressing, not absolute but, relative position in a series.

340. (2.) As regards the more electro-positive radicles. The terminations of their ordinary names are altered to *-ic*, and the names thus altered are placed before the names of the electro-negative radicles. Thus the name sodic chloride is assigned to common salt, a compound in which sodium is the electro-positive, and chlorine the electro-negative radicle. Potassic

* Exceptions to this rule are the sulphocarbonates, sulpharsenates, &c., radicles which are found on the type of known oxygen radicles, but contain sulphur in place of oxygen.

† The word 'atom' is here used in its chemical signification of 'the smallest quantity which can enter into chemical combination,' and not in its mechanical sense of that which is incapable of division.

‡ Or from the Latin: thus, *bi-*, *ter-*, *quadr-*, &c.

sulphate is the name of a compound of potassium with the sulphate radicle (a body which contains one atom of sulphur associated with four of oxygen). Hydric hypophosphite is the name of a compound of hydrogen with the lowest of the series of radicles containing phosphorus and oxygen.

341. When an electro-positive radicle unites in more than one proportion with an electro-negative radicle, the different compounds are distinguished either by a Greek prefix, such as *mono-*, *di-*, &c., or by giving the termination *-ous*, instead of *-ic*, to the name of the electro-positive radicle in the compound which contains the greatest proportion of it. This latter expedient is of course applicable only to cases where not more than two compounds are known. For instance, we know two compounds of chlorine and copper: the first, containing 127 parts of copper united with 71 of chlorine, is called cuprous chloride; the other, containing 63.5 parts of copper united with 71 of chlorine, is called cupric chloride. As an example of the other method, we may take the compounds in which the phosphate radicle is united with sodium and hydrogen in varying proportions. We have dihydric sodic phosphate, containing 2 atoms of hydrogen and 1 of sodium; hydric disodic phosphate, containing 1 atom of hydrogen and 2 of sodium; and trisodic phosphate, containing 3 atoms of sodium.

342. It may be remarked that, in forming these names, the Latin names of the elements are usually, but with a questionable gain as regards simplicity and intelligibility, taken instead of the English names. Thus the term argentic is often employed for compounds of silver, ferric for compounds of iron, plumbic for compounds of lead.

343. *Acids, Bases, Salts.*—These terms were formerly used in a much more precise sense than it appears possible to use them now. An acid was a sour (Lat. *acidus*) corrosive substance, soluble in water, which turned blue litmus-paper red, and which had a strong affinity for bases. A base was a substance which exhibited more or less of the properties of caustic potash, especially that of restoring the blue colour of litmus

which had been reddened by an acid. A salt was the substance formed by the union of an acid with a base, a substance usually crystalline and without action on litmus. Thus, sulphuric 'acid' possesses the above properties, and acts upon caustic soda, a 'base,' to form the neutral compound called Glauber's 'salt.' It will be noticed that the words are dependent upon each other, a 'base' being a substance which combines with an 'acid,' and *vice versa*; and modern research has shewn that many substances (especially among organic compounds) have a claim to be considered acids, although they only possess in common the last property mentioned above, namely, that of acting upon such a typical base as caustic soda or potash to form a neutral compound. At present, then, the term 'acid' is applied (when it is used at all) to a class of bodies which contain one or more atoms of hydrogen so combined as to be capable of being exchanged for an equivalent quantity of potassium or other typical basic radicle, the resulting compound being one capable of being classed with such a typical salt as sodic chloride. The so-called 'acid' is, in fact, a salt itself, the base of which is hydrogen, and the word 'base' is almost co-extensive in meaning with electro-positive radicle.

344. The word 'anhydride' is applied to a certain class of oxides which combine with water to form acids. Thus sulphuric trioxide is sometimes called sulphuric anhydride, since it combines with water to form sulphuric acid.

CHAPTER XII.

CHEMICAL NOTATION.

345. Chemists have agreed to represent, by means of symbols, certain weights of the substances with which they have to deal—namely, the weights of the smallest quantities of the elementary bodies which are found to be capable of being transferred from one compound to another in a chemical reaction ; in other words, the weights of their atoms.

346. Each of these symbols consists of one, or, at most, of two letters. The first of these is in every case (tungsten excepted) the initial letter of the name of the element ; not necessarily, however, its English name, except where that is identical with its Latin one. Thus the symbol for the potassium atom is not P, but K, from its Latin name Kalium ; the symbol for the lead atom is not L, but Pb, from the Latin Plumbum ; the symbol for the tin atom is not T, but Sn, from Stannum.

347. As several of the elementary bodies have names beginning with the same letter, it is necessary to find means of distinguishing their symbols from each other. Thus, the names of no fewer than nine of the elements begin with C. To the most important of them, carbon, the solitary initial letter is given as its symbol ; whilst the others, as the table shews (p. 136), have, in addition to the common letter, a vowel or consonant which occurs in their names, to distinguish them. Thus, the calcium atom is represented by the symbol Ca, the chlorine atom by the symbol Cl, the cobalt atom by the symbol Co. When we have constructed, on these principles, a series of symbols for the elementary bodies, we can readily express the molecules of compounds by placing in juxtaposition the symbols of the

elements which compose them, precisely as the letters which compose a word. Thus, CO represents the molecule of a compound substance consisting of single atoms of carbon and oxygen—namely, carbonic protoxide; KCl represents the molecule of potassic chloride, a compound of a potassium atom and a chlorine atom. Such a combination of symbols is called a formula.

348. When we have reason to believe that several atoms of an element are present in the molecule of any compound, instead of repeating the symbol, we attach to it, on the right and a little below it, a small numeral to denote the number of atoms present. Thus, the formula of the molecule of water is not written HHO, but H_2O ; the formula of ammonia is H_3N , not HHHN; and the formula of calcic chloride is $CaCl_2$, not CaClCl. It must be carefully noted that these small numerals only apply to the single symbol to which they are affixed, not to any other of the symbols in the formula. The only exception is where several symbols are enclosed within brackets, and the numeral is placed immediately after the bracket. In this case, each of the symbols within the bracket is to be considered as having the numeral attached to it. Thus, the formula for calcic nitrate is $Ca(NO_3)_2$, which is equivalent to CaN_2O_6 .

349. When two or more symbols are thus enclosed within brackets, it is intended to denote that the substance is a compound radicle, a group of atoms more intimately associated with each other than with the other substances present in the molecule, and capable of being transferred as a whole, in certain reactions, from one compound to another. For instance, in assigning to potassic nitrate, calcic nitrate, and ammoniac nitrate, the formulæ $K(NO_3)$, $Ca(NO_3)_2$, and $(H_4N)(NO_3)$, we imply that the molecules of these substances agree in structure in so far as they contain a radicle consisting of one nitrogen atom and three oxygen atoms, called the nitrate radicle.

350. An arrangement of symbols of this kind, in which an attempt is made to depict the structure of the molecule, is called a 'rational formula.' On the other hand, such a formula

as CaN_2O_6 , which merely gives the number of atoms in the substance, is called an 'empirical formula.'

351. When several molecules of a substance are to be expressed, a numeral is placed on the left of its formula, in the same position as an algebraic co-efficient. For instance, 2KCl represents two molecules of potassic chloride; $4\text{Ca}(\text{NO}_3)_2$ represents four molecules of calcic nitrate; the numeral in this case applying to the whole formula as far as the first comma, + sign, or full stop, and not simply to the symbol immediately following it.

352. The order of symbols in a formula is purely arbitrary. As a rule, the symbols of the more electro-positive atoms are placed first. The formula for water is written H_2O , and not OH_2 . This rule is not, however, rigidly observed in cases where a different order would render more clear the view taken of the structure of the molecule.

CHEMICAL EQUATIONS.

353. In order to give clearly and concisely the results of a chemical reaction, we employ a form of expression which resembles an algebraic equation. In this chemical equation we arrange, on the left hand of the sign =, the formulæ of the molecules which take part in the reaction, connecting them by the sign +; while, on the right hand, we place in a similar way the formulæ of the molecules which are the known products of the chemical change. The sign = signifies primarily that the sum of the weights of the molecules on each side of it are equal, a significance derived from the fact already mentioned (par. 280), that no weight is lost in a chemical change; in other words, that the products of a reaction weigh as much as the substances originally taken. But it implies more than this; it asserts that the molecules on the left hand can be broken up and converted into the molecules on the right hand.

354. For example, the equation



signifies that we can take 4 parts by weight (or 2 molecules) of

hydrogen, and 32 parts by weight (or 1 molecule) of oxygen, and cause them to react on each other, the product being $(4 + 32 =)$ 36 parts by weight (or 2 molecules) of water.

355. Similarly, the equation



signifies that, when we mix 100 parts by weight (or 1 molecule) of calcic carbonate with 73 parts by weight (or 2 molecules) of hydric chloride, the substances react on each other, and we obtain 111 parts by weight (or 1 molecule) of calcic chloride, 44 parts by weight (or 1 molecule) of carbonic dioxide, and 18 parts by weight (or 1 molecule) of water.*

. The importance of familiarising even very youthful students of chemistry with chemical notation cannot be overrated. It should be taught, however, to beginners gradually, and rather indirectly than formally. By the constant employment of the symbols and formulæ in explaining chemical changes to a class, the pupils rapidly become familiar with their use, and soon prefer to have changes explained by means of them. A single lesson will never demand reference to a great number of formulæ; and if the signification of each is explained when it is shewn, the discussion of the first four elements will supply a sufficient number of examples to enable this chapter to be completely understood.

The student should always be careful to use every chemical symbol in its proper sense only—namely, as an expression of a certain definite weight of a substance. A formula should not be used simply as a short-hand substitute for the name of the substance. Nothing can look more slovenly, often grotesque, than a description of an experiment, full of formulæ which cannot possibly, as they stand, be interpreted to signify definite weights, but appear to be solely introduced to save a few seconds of time, or a few millimetres of space. If our nomenclature is defective, it should be amended; but chemical symbols, no less than those of algebra, should be reserved for their own special uses.

In class-rooms, it will be found of great advantage to have a large

* In adding together the weights denoted by the symbols in a formula, it is convenient to place them as shewn below:

| | |
|---------------------|-----------|
| Ca = 40 | H = 1 |
| C = 12 | Cl = 35.5 |
| O ₂ = 48 | 36.5 |
| <u>100</u> | <u>2</u> |
| | 73.0 |

table of the elements, their symbols, and atomic weights, displayed at every chemical lesson ; and the various decompositions illustrated by symbols in succeeding portions of this volume should be gone over, step by step, on the black board by the teacher, and the pupil made to exercise himself on the same subject with his slate.

TABLE OF THE ELEMENTS, WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

Each line in the table should be read as in the following example: 'The aluminum atom is represented by the symbol Al, and weighs 27.5 times as much as the hydrogen atom.'

| Name of Element. | Atomic Symbol. | Atomic Weight. | Name of Element. | Atomic Symbol. | Atomic Weight. |
|----------------------------------|----------------|----------------|----------------------------------|----------------|----------------|
| Aluminum | Al | 27.5 | Molybdenum | Mo | 96 |
| Antimony (Stibium) | Sb | 122 | Nickel | Ni | 59 |
| Arsenic | As | 75 | Niobium | Nb | 94 |
| Barium | Ba | 137 | Nitrogen | N | 14 |
| Bismuth | Bi | 210 | Osmium | Os | 199 |
| Boron | B | 11 | Oxygen | O | 16 |
| Bromine | Br | 80 | Palladium | Pd | 106.5 |
| Cadmium | Cd | 112 | Phosphorus | P | 31 |
| Cæsium | Cs | 133 | Platinum | Pt | 197 |
| Calcium | Ca | 40 | Potassium (Kalium) | K | 39 |
| Carbon | C | 12 | Rhodium | Rh | 104 |
| Cerium | Ce | 92 | Rubidium | Rb | 85 |
| Chlorine | Cl | 35.5 | Ruthenium | Ru | 104 |
| Chromium | Cr | 52.5 | Selenium | Se | 79.5 |
| Cobalt | Co | 59 | Silicium or Silicon | Si | 28 |
| Copper (Cuprum) | Cu | 63.5 | Silver (Argentum) | Ag | 108 |
| Didymium | D | 96 | Sodium (Natrium) | Na | 23 |
| Erbium | E | 112 | Strontium | Sr | 87.5 |
| Fluorine | F | 19 | Sulphur | S | 32 |
| Glucinum | G | 9.5 | Tantalum or Co- lumbium | Ta | 182 |
| Gold (Aurum) | Au | 197 | Tellurium | Te | 129 |
| Hydrogen | H | 1 | Terbium (?) | ... | ... |
| Indium | In | 76 | Thallium | Tl | 204 |
| Iodine | I | 127 | Thorium | Th | 238 |
| Iridium | Ir | 197 | Tin (Stannum) | Sn | 118 |
| Iron (Ferrum) | Fe | 56 | Titanium | Ti | 50 |
| Lanthanum | La | 92 | Tungsten (Wolfram) | W | 184 |
| Lead (Plumbum) | Pb | 207 | Uranium | U | 120 |
| Lithium | Li | 7 | Vanadium | V | 51.25 |
| Magnesium | Mg | 24.5 | Yttrium | Y | 62 |
| Manganese | Mn | 55 | Zinc | Zn | 65 |
| Mercury (Hydrar- gyrus) | Hg | 200 | Zirconium | Zr | 89.5 |

CHAPTER XIII.

THE LAWS OF GASEOUS VOLUME.

SECTION I. MARRIOTTE'S LAW.

356. Several of the elementary bodies, and many of their more important compounds, are, at ordinary temperatures, gases, or may be converted into gases by the application of heat.

357. Bodies which assume the condition of elastic fluids at such a temperature as 15° C., are generally distinguished as *gases*, while those which require a higher temperature to convert them into elastic fluids, are called *vapours*. Thus oxygen is called a gas, steam a vapour.

358. There is no distinction, however, of kind, but only one of degree, between a gas and a vapour. They differ from each other only in so far as the one requires a different amount of heat from the other to maintain it as an elastic fluid. A vapour may be called an easily condensed or temporary gas; a gas, a highly incondensable or permanent vapour. The classes of gases and vapours shade away insensibly into each other, so that no sharp line of demarcation can be drawn between them.

359. Gases are measured in cylindrical glass vessels or jars, open at one end, and shut at the other, the sides of the jar being marked with lines, denoting how many cubic centimetres of gas the vessel can contain. When such a jar is used as a measure, it is filled with water or



Fig. 26.

quicksilver, and placed standing with its mouth down in a basin or trough, containing the same liquid. The gas to be measured is then passed up through the water or quicksilver, which it displaces more or less, occupying its room, and filling, according to the amount of liquid displaced, a larger or smaller portion of the vessel. The number of cubic centimetres to which it amounts is then ascertained, by noting the figure marked upon the graduated jar, at the line where the gas and liquid meet.

360. This observed volume, however, requires several corrections. In the first place, since, as has been already explained (par. 104), gases expand or occupy a greater space when heated, and contract or fill a smaller space when cooled, it is necessary, when making comparative experiments, to examine each gas at the same temperature. The usual temperature to which all volumes of gases are reduced is 0° C., and the method of making these corrections is explained in par. 106.

361. In the next place, it is found that gases alter their volume when the pressure upon them is changed, and we shall see that this variation takes place according to a law no less simple and universal than that which expresses the variation of the volume of a gas with temperature.

362. It must be borne in mind that gases are almost always measured under the pressure of the atmosphere, which varies slightly from time to time, and is ascertained by observing the height of the column of mercury which it will support in the tube of a barometer. Thus, in saying that the average pressure of the air in our latitudes is 760 millimetres, we mean that the top of the mercury column oscillates a little above or below that height above the level of the mercury in the cistern.

363. In order to investigate the effects of pressure upon a gas, we must have some means of adding to or taking from this atmospheric pressure. The fact that gases do vary in volume under changed pressure may be shewn by placing a small balloon of gold-beater's skin, containing a little air, under the receiver of an air-pump, and exhausting the air. As the exhaustion proceeds, the balloon will become distended, and

when air is readmitted to the receiver, the balloon will shrink again to its original condition. This we find to be the case whatever gas the balloon contains, and hence we infer that all gases expand when the pressure on them is diminished, and contract when the pressure on them is increased.

364. In order to determine the rate of the variation, we may have recourse to an apparatus in which the pressure is applied by means of a column of mercury of variable length. Such an apparatus is shewn in fig. 27. It consists of a tall wooden frame on which is fixed a cylindrical tube, A, about 2 cm. in diameter, and 45 cm. in length, having a glass stop-cock at the top, through which gas may be introduced. The lower end of this tube is connected by a flexible india-rubber tube,* with a jar of mercury, B, suspended by a cord passing over a pulley at the top of the frame, and having a counterpoise at its other end, behind the frame. There is a scale attached to the gas-tube for ascertaining the volume of the enclosed gas, and a movable scale (not shewn in the figure) is placed between the tube and the jar, for the purpose of measuring the differences of level of the mercury.

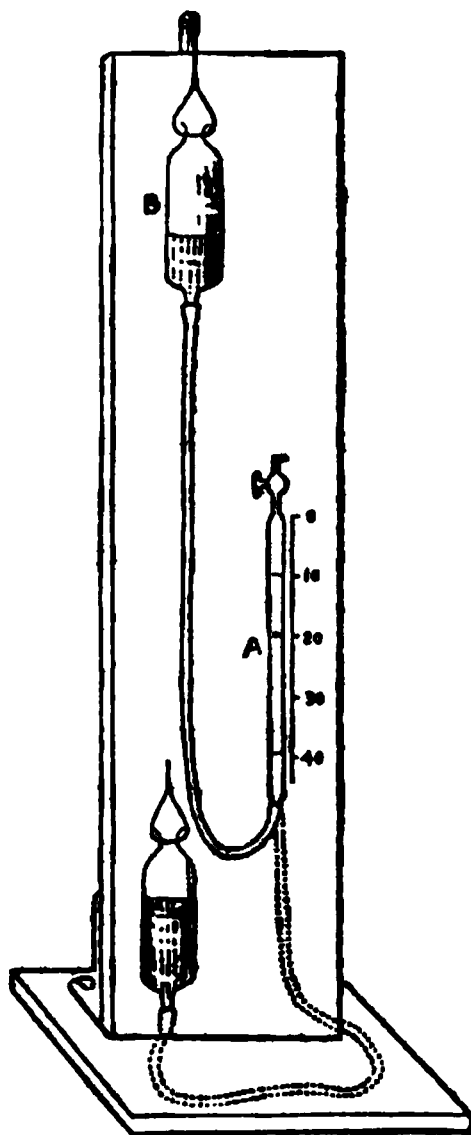


Fig. 27.

365. In the first place, let the tube be filled with any gas, such as oxygen, to the 20th division on the scale, the jar being lowered until the mercury in it stands at the same level as in the tube: the glass stop-cock is then closed. The gas in the tube is now exposed to the pressure of the air alone (acting

* The common vulcanised tubing is too porous to be of any use in this apparatus. The tube must be of the black tubing, strengthened either by having a case of strong linen sewn closely over it, or by having a similar layer incorporated with it during manufacture, as in the ordinary water-hose.

through the column of mercury in the flexible tube), which we will assume to be 760 mm. Next, let the jar be raised until the mercury in it stands 760 mm. above the level of the mercury in the tube, the movable scale being raised as required. We shall now find that the mercury in the tube stands at the 10th division. The volume of the gas is, in fact, reduced to one-half. But the column of mercury, 760 mm. high, is equivalent to the pressure of an additional atmosphere; in other words, the whole pressure on the gas is that of two atmospheres, or twice what it was at the beginning of the experiment. By doubling the pressure we have reduced the volume of the gas to one-half.

366. In the next place, let the jar, B, be lowered until the level of the mercury in it stands 380 mm. below that of the mercury in the tube. We shall find that the gas which at first occupied 20 divisions now occupies 40. Its volume has been doubled. The atmospheric pressure is here partly counterbalanced by the column of mercury in the tube, which is 380 mm. high, or exactly one-half of the whole column which the atmosphere can support. The pressure, then, on the gas is represented by the remaining half of the atmospheric pressure, or one-half its original amount. Thus, by reducing the pressure to one-half, we have doubled the volume of the gas.

367. Other trials may be made at intermediate pressures, or at higher and lower ones, and will serve to confirm the following statement of the law:

THE VOLUME OF A GAS VARIES INVERSELY AS THE PRESSURE UPON IT.*

368. This law, which was first established by the Abbé Marriotte, a Frenchman, and by Boyle, the great English

* That is, a pressure of 2, 3, 4, &c. times the original amount, will reduce a gas to $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, &c., its original volume.

Let V = the original volume of the gas, under a pressure P .

V' = its volume under another pressure P' .

Then $V : V' :: P' : P$.

Or $V' = V \frac{P}{P'}$.

chemist, is found to hold good for all the permanent gases—namely, oxygen, hydrogen, nitrogen, carbonic oxide, nitric dioxide, and marsh-gas. When, however, a condensable gas is taken, such as sulphuric dioxide, it is found to yield to pressure more than the law requires, and this deviation increases as the pressure approaches nearer to that under which the gas liquefies, until the latter suddenly collapses into a liquid, which again expands into a gas as soon as the pressure is lessened.

369. The force with which an elastic fluid, such as a gas, resists compression is called its 'tension.' It obviously increases with the pressure, and is expressed by stating the pressure—for instance, the column of mercury which the gas will support. Thus, when oxygen is submitted to a pressure of 2 atmospheres,* its tension is said to be twice as great as its tension under 1 atmosphere. Since, as we have seen (par. 104), a gas tends to expand by heat, if we prevent its expansion by heating it in a closed non-elastic vessel, its tension will be increased, and will vary with the temperature. A gas which is just becoming liquid is said to be at its 'point of maximum tension.'

370. We have two methods, then, of reducing a gas to a liquid: either (1), we may, keeping the temperature constant, increase the pressure until the point of maximum tension is reached; or (2), we may lower the temperature, and with it the point of maximum tension, until the latter falls below the pressure to which the gas is exposed. Some gases, such as sulphuric dioxide, cyanogen, and ammonia may be easily liquefied by either method; but it is generally advantageous to combine the two, to lower the temperature, and at the same time to increase the pressure. By these means, Faraday and others have succeeded in liquefying all known gases, except the six above mentioned; and by a further reduction of temperature many liquefied gases have been reduced to the solid form. But no gas has been solidified by pressure alone.

* By the term 'atmosphere,' in speaking of pressures, is meant a pressure equal to that of a column of mercury 760 mm. in height.

371. A short table of the maximum tensions of a few gases is given below :

| Temperature. | Maximum Tension of | | |
|--------------|--------------------|-----------------|-------------------|
| | Sulphuric Dioxide. | Ammonia. | Carbonic Dioxide. |
| Centigrade. | Mm. of Mercury. | Mm. of Mercury. | Atmospheres. |
| 0° | 1480 | 3610 | 38.5 |
| 10° | 2390 | 4980 | 52 |
| 15° | 2930 | 5780 | 56 |
| 20° | 3540 | 6674 | 64 |

372. Let us now return to Marriotte's law. We learn from it that in measurements of gases it is no less necessary to note the pressure than the temperature to which they are exposed ; and we also learn an easy method of reducing volumes of gases measured at any given pressure to the volumes at the standard pressure, 760 mm. The ratio is expressed as follows : As 760 is to the observed pressure in millimetres, so is the observed volume to the volume the gas would occupy at the standard pressure. In other words, multiply the observed volume by a fraction of which the observed pressure is the numerator, and 760 is the denominator.

373. To take an example. A volume of oxygen was found to measure 25 c.c. at a pressure of 670 mm. Then $\frac{670}{760} \times 25$ c.c. = 22.04 c.c., which is the volume which the gas will measure at the standard pressure.

374. Such a correction is always required in practice when the level of the mercury in the measuring jar, fig. 27, is not the same as the level of the mercury in the trough. For this difference of level indicates a certain pressure added to, or subtracted from the barometric pressure at the time. If, as is usually the case, the level of the mercury in the jar is above that in the trough, the gas is exposed to a less pressure than that of the atmosphere, since the latter is partly counter-balanced by the column of mercury in the jar. We must

therefore measure the height of this column, and subtract it from the height of the barometric column, before making the above calculation.

375. The following example of an actual reading will serve to illustrate the complete reduction of an observed volume of a dry gas :

- a.* Observed volume of gas (dry)..... = 140.5 c.c.
- b.* Height of mercury in tube above that in trough... = 10 mm.
- c.* Height of barometer..... = 748 mm.
- d.* Temperature of room..... = 15° c.

Subtracting *b* from *c*, we have 738 mm. as the pressure under which the gas was measured. Then $\frac{738}{760} \times 140.5 \text{ c.c.} = 136.4$, which is the volume of the gas under 760 mm. pressure. But, as explained in par. 106, a gas which measured 1 c.c. at 0° would become $(1 + .00366 \times 15 =) 1.055$ c.c. at 15°. Hence, $1.055 : 1 :: 136.4 : 129.29$. The volume of the gas therefore at 0° and 760 mm. will be 129.29 c.c.*

SECTION II. AMPERE'S LAW.

376. By the methods given in the last section, we can calculate the weight of any given volume of a gas if we know (1) its density (par. 61), and (2) the weight of 1 c.c., at the standard pressure and temperature of the gas which is taken as the unit of density.

377. For instance, if it is required to ascertain the weight of 1 litre of hydrogen, at the standard pressure and temperature, we proceed as follows : The density of hydrogen referred to air is 0.0693. The weight of 1 c.c. of air, at 0° C. and 760 mm., is 0.001293 gm. Hence the weight of 1 litre of air is 1.293 gm. Then :

$$\begin{array}{ccccccc} \text{Density of air} & : & \text{Density of hydrogen} & :: & \text{Wt. of 1 litre of air} & : & \text{Wt. of 1 litre of hydrogen.} \\ 1 & : & 0.0693 & :: & 1.293 \text{ gm.} & : & 0.0896 \text{ gm.} \end{array}$$

* If the gas is not dry, but saturated with moisture, a further correction must be made for the tension of the aqueous vapour, which acts in depressing the column of mercury in the tube, and thus in increasing the apparent volume of the gas. Tables of the tension of aqueous vapour in millimetres of mercury will be found in most treatises on physics, and the number corresponding to the temperature must be added to the height of the column of mercury in the tube, and the whole subtracted from the barometric column.

378. The weights of 1 litre of several gases are given in the second column of the table below; while in the third column are given the densities of the same gases, referred to hydrogen as the unit, instead of air.

| Name of gas. | Weight of 1 litre. | Density (hydrogen = 1). | Weight of molecule (hydrogen atom = 1). |
|----------------------|-----------------------|----------------------------|--|
| Hydrogen | 0.0896 gm. | 1 | 2 |
| Oxygen | 1.430 " | 16 | 32 |
| Nitrogen | 1.256 " | 14 | 28 |
| Carbonic oxide | 1.256 " | 14 | 28 |
| Nitrous oxide..... | 1.971 " | 22 | 44 |
| Steam..... | 0.805 " | 9 | 18 |

379. It is impossible not to be struck by the correspondence of the numbers in the third column with the atomic weights given in the table at p. 136. A litre of oxygen, for instance, weighs 16 times as much as a litre of hydrogen, and the weight of the oxygen atom is believed to be 16 times as great as the weight of the hydrogen atom. A similar correspondence is observed in the case of almost all elementary gases. In the case of the compound gases, another but almost equally simple relation appears. The weight of a litre of carbonic oxide is 14 times as much as that of a litre of hydrogen, and the weight of the molecule of carbonic oxide (represented by the formula CO) is 28, or 14×2 times as much as the hydrogen atom. In fact, we find that the following rule holds good for almost all gases: 'If hydrogen is taken as the standard, both of weight and density, the densities of elementary gases are identical with their atomic weights; the densities of compound gases are one-half their molecular weights.'

380. Now this sharp distinction between compound and elementary gases disappears entirely, if we consider that the molecule (par. 310) of an element is composed, in general, of two atoms of the element. The molecule of hydrogen (represented by H_2) will then be twice the weight of the hydrogen atom; the molecule of oxygen (represented by O_2) will be 32 times the weight of the hydrogen atom; of carbonic oxide, 28 times, &c., and so on, as given in the fourth column of the

above table. We may then comprehend nearly all gases, whether simple or compound, in the following statement: 'The weights of equal volumes of all gases are in the same ratio as the weights of their molecules.'

381. These observed facts did not fail to suggest to Ampère the hypothesis that a certain measure, say 1 litre, of any gas whatever contains the same number of molecules of the substance, or, as his law is generally expressed:

THE MOLECULES OF ALL SUBSTANCES ARE OF THE SAME SIZE, WHILE THEY DIFFER IN WEIGHT.

382. The following illustration may serve to make this clearer: Take three glass tubes of the same internal diameter and of the same length, closed at one end. Place in one a certain number, say 10, india-rubber balls; in another, the same number of glass 'solitaire' balls, of the same size as the india-rubber balls; in the third, the same number of similar leaden bullets. Then these balls may represent the molecules of different substances in the gaseous state. The three equal-sized tubes will contain equal numbers, and the weights of the whole will obviously be in the same ratio as the weights of one india-rubber, glass, and leaden ball respectively.

383. Enough has been said in the chapter on Heat, and in the preceding section of this present chapter, to shew the high probability on physical grounds that gases are similar in constitution. All gases vary in volume under changes of pressure and under changes of temperature according to the same law.

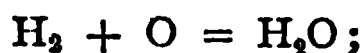
384. The above law only applies to gases. No such simple expression can be found for the molecular volume of liquids and solids. In these conditions the molecules are much nearer each other, and are more subject to the disturbing forces of cohesion, polarity, &c. Nevertheless, certain well-marked correspondences have been found to exist between the molecular weight and the density of several groups of substances—for instance, selenium and sulphur, gold and silver, the alums.

385. The following considerations will suggest themselves from what has been said :

(1.) The density of a substance in the state of gas, referred to hydrogen as the unit, will indicate the weight of its molecule referred to the hydrogen molecule as the unit. The importance attached to this criterion of molecular weight is very great; only the strongest chemical reasons are allowed to set it aside.

(2.) The molecules of a highly complex substance must consist of a cluster of atoms in much closer proximity than those of a simpler substance. No matter how many atoms go to form the molecule, they are in all cases condensed into the same space.

(3.) If the molecules of the elements are compound in structure, consisting, in general, of two atoms of the element, we must be careful to describe every reaction in which an element takes part, in such a way as to shew that two atoms of it are concerned. Thus, in the equation expressing the formation of water, we must not write :



but



When equations are thus consistently written, they may be interpreted to express chemical changes by volume as well as by weight. Thus, the above equation expresses the fact that two measures of hydrogen unite with one measure of oxygen to form two measures of water-gas or steam.

(4.) The extremely simple ratios in which gases combine are explained on the above view. It has long been observed that combination by volume takes place in the proportion of 1 : 1 (as in the case of chlorine and hydrogen), 1 : 2 (as oxygen and hydrogen), 1 : 3 (as nitrogen and hydrogen), &c., the product in all these cases occupying the same volume, 2. This could not but happen if the action was between molecule and molecule (generally a small number being concerned), and if all such molecules were the same size.

CHAPTER XIV.

ATOMIC WEIGHTS—ATOMICITY.

SECTION I. THE DETERMINATION OF ATOMIC WEIGHTS.

386. It is intended in the present section to indicate the principles on which, assuming the truth of Ampère's law, the atomic constitution of substances may be arrived at with a high degree of probability. It is obvious that, since the single atoms themselves are beyond the reach of our senses, the problem consists in determining the relative weight of them.* This we can ascertain without isolating a molecule or atom, by measuring and weighing masses of them, just as we can ascertain the *proportion* of silver and copper in a single shilling quite as accurately by analysing a mass of shillings as by analysing one shilling, supposing that we had not weights small enough to give us the weight of a single shilling.

387. We may take, as our first example, the inquiry into the constitution of the molecule of water. The results of analysis inform us that, from one litre of water gas or steam we can obtain one litre of hydrogen gas and half a litre of oxygen. We are, then, justified, on Ampère's hypothesis, in considering (1) that a certain number of molecules of water yield the same number of molecules of hydrogen, and half the number of molecules of oxygen; (2) if the molecules of these elements are

* A case not dissimilar is found in the science of astronomy. The *relative* distances of the planets and their satellites were known with considerable accuracy long before their absolute distances were arrived at by the measurement of one distance—that of the earth to the sun.

similarly constituted, that the molecule of water consists of a certain number of hydrogen atoms associated with half the number of oxygen atoms.

388. The next question which arises will be, what is the actual number of hydrogen and oxygen atoms in the molecule of water? Now, when a litre of steam is acted on by the metal sodium, only half a litre of hydrogen gas is obtained, the rest of the hydrogen, together with the whole of the oxygen, forming a compound with the sodium, called sodic hydrate (caustic soda). Further, when we examine and analyse this caustic soda, we find that we can take out from it (by acting upon it with more sodium), not half at a time, but all the hydrogen it contains, a compound being left, which contains sodium associated with all the oxygen which was in the original litre of water.

389. We gather from this and many analogous experiments, that we can divide the hydrogen contained in a litre of steam into two and only two equal portions, measuring half a litre each, while the oxygen cannot, so far as is known, be thus divided—it must be taken out altogether, when it is taken out at all.

390. Further, if we take any substance containing oxygen which can be examined in the state of gas, and subject it to analysis, we find that from a litre of the vapour of no substance whatever can we obtain less than half a litre of oxygen. The same is found to be true of substances containing hydrogen. We know of no compound containing hydrogen from a litre of the vapour of which we obtain less than half a litre of hydrogen. This law is observed to be so uniformly true that we may feel justified in extending it to bodies containing oxygen, and those containing hydrogen, which we have not been able to examine in a state of vapour.

391. The inferences which we seem entitled to draw are :

(1.) That the quantity of oxygen which enters into the composition of the molecule of water is the smallest quantity which enters into the composition of any molecule whatever—in other words, is the atom of oxygen.

(2.) That, since the quantity of hydrogen in the molecule of water can be divided into two, and only two parts, one of these parts is the atom of hydrogen.

392. This will serve to indicate the course by which the number of atoms of an element in any compound is ascertained. If we find that we can take out the element only as a whole, and not, by successive steps, one half, one third, &c. of it, then we conclude that only one atom is present in the molecule of that compound. In fact, putting theory apart, the atom may be represented by the least quantity of an element which we can take out from any of its compounds.

393. Now, when a litre of the vapour of any compound whatever is submitted to examination, it is found that, with scarcely any exceptions, we never obtain from it less than half a litre of any of the elementary substances contained in it—that is, a volume equal to that of the oxygen which was obtained from a litre of steam. In a word, the smallest quantity of any element whatever which can be obtained from a compound occupies the same volume when in the state of gas. And although we have no conception whatever of the actual number of atoms which this volume contains, yet it may represent the atom; and the relative weights of these half-litres, which are obviously the densities of the gases, will also express the relative weights of the atoms. A short table of the atomic weights which have been ascertained in this way will be found at p. 156.

394. There is, however, a serious difficulty attending the determination of the atomic weights of many substances—namely, that we cannot examine them in the state of gas. We cannot, for example, obtain carbon as a gas in order to compare its vapour-density with that of hydrogen. In such cases, and they are unfortunately the majority, we have to resort to other, and often less conclusive methods for ascertaining the atomic weight of the substance. One of such methods is the following:

395. We endeavour to form a compound of the substance—for instance, carbon—which we can examine in the state of gas, the other constituents of which compound have had their

atomic weights previously determined. We find the weight of a litre of this compound, and observe what volume we can obtain from it of the elements which are combined with the carbon. If the chemical examination of the compound leads us to conclude that the carbon in it cannot be divided, cannot be taken out in two or more instalments (like the hydrogen in water), then we have reasons for believing that one litre of the compound would yield half a litre of carbon gas, and, therefore, that the weight of carbon obtainable from it is the weight of half a litre of carbon gas, and expresses, when compared with the weight of half a litre of hydrogen, the weight of the atom of carbon.

396. For instance, we know a substance called carbonic dioxide, from a litre of the vapour of which we can obtain a litre of oxygen weighing 1.430 gm., and a quantity of carbon weighing 0.536 gm. We also know a substance called hydrocyanic acid (hydric cyanide), from a litre of the vapour of which we can obtain half a litre of hydrogen, half a litre of nitrogen, and a quantity of carbon weighing 0.536 gm. In neither of these compounds is the carbon, so far as we know, divisible into several parts : it is taken out of the substance as a whole, and not by instalments. We therefore conclude that the carbon obtainable from a litre of carbonic dioxide, or of hydric cyanide, would, in a state of gas, measure half a litre, its weight being 0.536 gm. And since this is twelve times the weight of the same volume of hydrogen, it is inferred that the atom of carbon is twelve times as heavy as the hydrogen atom.

397. There are many cases in which even the above method is inapplicable, as we have not been able to examine any stable volatile compounds containing the element. In such cases, we are obliged to rely upon the results of weight alone, irrespective of volume. We take a compound formed by the element in question with another element, the atomic weight of which is well ascertained, and which compound, from its properties, appears to contain one atom, or at anyrate a known number of atoms of its constituents. We obtain by analysis its composition

by weight. If we have reason to believe that there is a single atom of each of its constituents present in a molecule, then the numbers obtained will at once express the relative weights of these atoms, which are for convenience reduced to the standard hydrogen unit. If there are supposed to be several atoms present, then we divide the weight of each element found by the number of atoms of it present, and the quotient will give, as before, the relative weights of the single atoms.

398. For instance, we have never been able to examine barium, or any of its compounds, in a state of vapour. But we know a compound of it with chlorine, the molecule of which is believed to contain one atom of barium united with two of chlorine. This substance is found to contain per cent. :

| | |
|---------------|-------|
| Barium..... | 65.9 |
| Chlorine..... | 34.1 |
| | <hr/> |
| | 100.0 |

Dividing the amount of chlorine by 2, we obtain 65.9 : 17.05 as the relative weights of the atoms of chlorine and barium. Now, it is pretty certain that the atom of chlorine is 35.5 times as heavy as the hydrogen atom. Hence, by the proportion :

$$17.05 : 35.5 :: 65.9 : 137.2,$$

the barium atom is 137.2 times as heavy as the hydrogen atom.

399. Besides the above methods, we have another purely physical criterion to aid us in determining atomic weights—namely, Dulong and Petit's law of atomic heats, which is given in par. 141 (p. 55). This law holds good so invariably, that when other experiments point to atomic weights which would be at variance with it, we look upon them as being at least uncertain. For instance, the atomic weight of copper was for a long time assumed to be 31.7. But it has been found that the amount of heat required to raise 31.7 kilogrammes of copper 1° C. is only half as much as is required to raise 1 kilogramme of hydrogen to the same temperature. This, among other reasons, has led chemists to adopt 63.4, and not 31.7, as the weight of the copper atom.

400. We have, in the last place, to examine certain exceptions to the general law that the smallest quantity of an element which we can obtain from a litre of the vapour of compounds containing it, is half a litre.

401. (*A.*) It is found that the smallest quantity of phosphorus which can be obtained from a litre of one of its compounds (for example, phosphorous trichloride), is one-fourth of a litre, and not half a litre, as the law requires. We must hence infer one of two things :

(*a*) Either, the phosphorus molecule is only one-half the size of the hydrogen molecule ;

(*b*) Or, four phosphorus atoms are clustered together in the molecule, and are packed into the same space as two hydrogen atoms.

The latter supposition is by far the most probable. It preserves the integrity of the hypothesis that all molecules are of the same size, and only forbids us to assume that all elementary molecules are made up of the same number of atoms, a law which we have no right to consider absolute. Arsenic presents the same anomaly as phosphorus.

402. It is worth mentioning, that sulphur compounds (such as sulphur dioxide) yield, for a litre of vapour, a quantity of sulphur, which at 700° C. and lower temperatures, only measures one-sixth of a litre. But at 900° C., this quantity of sulphur vapour suddenly expands until it occupies the normal space of half a litre. It is possible that the phosphorus vapour may, at some temperature, expand in the same way, but this has not yet been realised experimentally. It may also be observed that all three substances, phosphorus, arsenic, and sulphur, are remarkable instances of allotropy—that is, that they can exist in forms which, though chemically identical, differ greatly in physical properties ; a fact which seems to shew that they are susceptible of great differences in atomic structure.

403. (*B.*) From a litre of no compound containing mercury can we obtain less than a litre of mercury vapour. From this we must infer :

- (a) Either, that two atoms of mercury are united so closely in its compounds that we have never been able to separate them, even so as to transfer one single atom of mercury from one compound to another;
- (b) Or, that the atom of mercury is as large as the molecule of hydrogen, and can, like the latter, and unlike the atoms of many other bodies, exist in a free state.

The same is true of cadmium, zinc, and a number of other metals, if we take into account, as we seem compelled to do, the strong analogies which exist between them, and which have been most cogently stated by Professor Würtz.

404. This is by far the most serious class of exceptions to the law, and no adequate explanation of them has yet been given. It may be that, just as sulphur vapour was originally measured and weighed at too low a temperature, so mercury vapour is measured and weighed at too high a temperature, at a temperature which does not permit the atoms to approach each other so closely as that the molecule may assume its normal size. This, as we shall see, is an explanation which is thought sufficient to account for a similar anomaly in certain compound gases. But we have no experimental evidence to support it in the present instance.

405. There are, finally, a few compound substances, the composition of the molecules of which, as determined by chemical considerations, differs from that obtained from physical data. Thus, one litre of nitric oxide yields half a litre of nitrogen and half a litre of oxygen; and we should hence infer, consistently with our hypothesis, that the molecule of it contained one atom of nitrogen and one atom of oxygen. But almost all other considerations (for example, its place in the series of nitrogen oxides) lead us to the conclusion that its molecule contains two atoms of nitrogen associated with two atoms of oxygen, in which case one litre of it should yield one litre of nitrogen and one litre of oxygen. It would appear, then, that at the temperature at which the gas has been examined, the molecule is twice as large as it ought to be, and that one

litre contains only half as many molecules as a litre of other gases.

406. Again, a litre of the vapour of ammoniac chloride yields only a quarter of a litre of nitrogen; and the same quantity of chlorine, together with one litre of hydrogen; while an examination of the chemical properties of the substance makes it almost certain that its molecule contains one atom of nitrogen, one atom of chlorine, and four atoms of hydrogen, so that we should expect a litre of its vapour to yield half a litre of nitrogen, half a litre of chlorine, and two litres of hydrogen. Further, a litre of the vapour of hydric sulphate yields only half a litre of hydrogen, although we have abundant reason for believing that its molecule contains two atoms of hydrogen.

407. It will be observed that in all these instances the anomaly is in the opposite direction to that of phosphorus, arsenic, &c. In the latter case, the molecule is apparently too small; in the present instance, it is apparently too large. And just as, in the case of phosphorus, the difficulty is met by supposing that the atoms are nearer each other than usual, so here it is possible to conceive that the atoms composing the molecule are further apart from each other, so that the system or molecule occupies more space than usual, at the temperature at which the substance has been examined. Thus, in the molecule of nitric oxide, we may have two atoms of nitrogen and two atoms of oxygen, united, indeed, but not condensed.

408. This view is much strengthened by the consideration of another case of similar anomaly—namely, that of nitric tetroxide. This body, which boils at 22° C., is found, when a litre of its vapour is examined at 100° C., to yield only half a litre of nitrogen and one litre of oxygen, although we have the same reasons, as in the case of the dioxide, for believing that its molecule contains two atoms of nitrogen and four atoms of oxygen. But experiments made (*Q. J. Chem. Soc.*, xv. 196) upon its vapour at much lower temperatures, shew that, at or near 24° C., a great contraction takes place, as in the case of

sulphur, and lead us to believe that at low temperatures the vapour may occupy only half its volume; in which case, of course, one litre would yield one litre of nitrogen and two litres of oxygen, as for many reasons we expect it to do.

409. It would appear, in fact, that nitric tetroxide, and probably also the other substances which have been mentioned, can exist in more than one state of condensation; that precisely as the planets in a system may conceivably have their orbits contracted in diameter without losing their character as a system, so the atoms in a molecule may approach each other more closely so as to reduce the molecule to a fraction of its former size; or, on the other hand, may recede from each other so as to double the size of the molecule, without altering its chemical properties.

410. It has been thought that the molecule in its expanded state is actually decomposed, and that its constituents exist free and uncombined in the vessel containing them, again passing into combination as the temperature falls. And it has been found possible to separate (for instance) hydric sulphate vapour into water and sulphur trioxide, by mechanical means, that is, by diffusion, pointing to the conclusion that these substances are in a state of mechanical mixture at a temperature of 400° C. But this supposition scarcely seems necessary. We find such great variations in the volume occupied by a given weight, in the case of the different allotropic forms of some of the elements, that there seems no reason why the same may not be true of compounds. The bond of chemical affinity may be much enfeebled, but it is not necessary to suppose it broken.

TABLE OF THE ATOMIC AND MOLECULAR WEIGHTS OF THE ELEMENTS WHICH HAVE BEEN EXAMINED IN THE STATE OF VAPOUR.

| Name. | Weight of 1 Litre. | Density (Hydrogen = 1). | Weight of | |
|-----------------|-----------------------|----------------------------|----------------------------------|------|
| | | | Molecule (Hydrogen atom = 1). | Atom |
| | grms. | | | |
| Hydrogen | 0.0896 | 1 | 2 | 1 |
| Nitrogen | 1.256 | 14 | 28 | 14 |
| Oxygen | 1.430 | 16 | 32 | 16 |
| Sulphur | 2.867 | 32 | 64 | 32 |
| Selenium | 7.025 | 79.5 | 159 | 79.5 |
| Tellurium | 11.535 | 129 | 258 | 129 |
| Chlorine | 3.173 | 35.5 | 71 | 35.5 |
| Bromine | 6.999 | 80 | 160 | 80 |
| Iodine | 11.361 | 127 | 256 | 127 |
| Phosphorus.... | 5.542 | 62 | 124 | 31 |
| Arsenic | 13.408 | 150 | 300 | 75 |
| Cadmium | 5.006 | 56 | 112 | 112 |
| Mercury | 8.959 | 100 | 200 | 200 |

SECTION II. ATOMICITY.

411. It is possible by the methods indicated in the last section to arrive at a knowledge, more or less complete, of the composition of the molecule of most substances. But the chemist aims at more than this; he desires to know, not only how many atoms and of what kind make up the molecule, but also how they are arranged in the molecule; he investigates its structure as well as its composition.

412. We know so little, however, of the real nature and mode of working of chemical affinity, that this part of the subject admits of far less satisfactory demonstration than other parts. We have often to leave the firm ground of experimental results, and to depend upon reasoning from analogies and probabilities of very uncertain value.

413. It is observed that large groups of substances behave in a similar way when treated by the same methods: they are formed by analogous operations, they are decomposed by similar means. Thus the group of the chlorides may almost all be formed by the direct union of chlorine with other radicles, and they all yield chlorine when acted upon by oxidising agents: they are also, in general, isomorphous. We hence infer a general similarity of structure in their molecules; we consider that there is a distinct line of separation (what in crystallography would be called a 'plane of cleavage') between the chlorine and the other constituents of the molecule. We can, for instance, take out the hydrogen from a molecule of hydric chloride, and put another radicle in its place, without altering the atomic structure of the compound.

414. A like relationship is observed in the compounds called oxides, nitrides, carbides, &c. We know of compounds of all these radicles with hydrogen, from which we seem able to take out the hydrogen, replacing it by other substances more or less kindred in nature. In the chapter on Electricity, several instances of such replacement have been given; and, indeed, nearly all compounds may be regarded as derivable by a process of substitution from some one typical member of the group.

415. But when we inquire in what proportion this combination of other substances with, for instance, chlorine, oxygen, nitrogen, and carbon, takes place, we find a great difference in the case of different radicles. This will be best shewn by comparing together the compounds of the above radicles with hydrogen, which many reasons lead us to take as the unit of chemical equivalency.

416. The composition of four typical compounds of hydrogen are given below:

| | |
|----------------------|------------------|
| Hydric Chloride..... | HCl |
| Water..... | H ₂ O |
| Ammonia..... | H ₃ N |
| Marsh-gas..... | H ₄ C |

and we gather that while an atom of chlorine requires only 1 atom of hydrogen to form a stable compound, an atom of oxygen requires 2; an atom of nitrogen, 3; and an atom of carbon, 4 atoms of hydrogen. We may also represent these compounds as formed by a process of substitution from one or more molecules of hydrogen. Thus:

| 1 Molecule. | 2 Molecules. | 3 Molecules. | 4 Molecules. |
|-------------|--------------|--------------|--------------|
| HH | HH | HH | HH |
| — | HH | HH | HH |
| HCl | — | HH | HH |
| | H } O | — | HH |
| | H } | H } N | — |
| | | H } | H } |
| | | H } | H } |
| | | | H } C |

In hydric chloride, one hydrogen atom is replaced by one of chlorine; in water, two atoms by one of oxygen; in ammonia, three atoms by one of nitrogen; in marsh-gas, four atoms by one of carbon.

417. It is generally believed that this points to a real difference of chemical power, of saturating capacity in the radicles chlorine, oxygen, nitrogen, and carbon respectively; and it is this difference which is expressed in the term 'atomicity.' Radicles are divided into classes according to the number of hydrogen atoms to which they are equivalent, or which they can replace; such equivalency being indicated by dashes, ', placed after the symbol or formula. The following are examples of the principal classes formed on the above principle.

(1.) Monatomic radicles, which replace 1 atom of hydrogen :

| Name. | Atomic Formula. | Example. |
|----------------|------------------|--|
| Chlorine..... | Cl | HCl', Hydric Chloride. |
| Cyanogen..... | CN | H(CN)', Hydric Cyanide. |
| Potassium..... | K | K'Cl, Potassic Chloride. |
| Ammonium..... | H ₄ N | (H ₄ N)'Cl, Ammonic Chloride. |

(2.) Diatomic radicles, which replace 2 atoms of hydrogen :

| Name. | Atomic Formula. | Example. |
|--------------------------------------|-----------------|---|
| Oxygen.....O | | $\text{H}_2\text{O}''$, Water. |
| Sulphuryl..... SO_2 | | $(\text{SO}_2)''\text{O}$, Sulphuric Trioxide. |
| Copper.....Cu | | $\text{Cu}''\text{O}$, Cupric Oxide. |
| Ethylene..... H_4C_2 | | $(\text{H}_4\text{C}_2)''\text{Cl}_2$, Ethylenic Dichloride. |

(3.) Triatomic radicles, which replace 3 atoms of hydrogen :

| | | |
|-------------------|--|--|
| Nitrogen.....N | | $\text{H}_3\text{N}'''$, Ammonia. |
| Bismuth.....Bi | | $\text{Bi}''' \text{Cl}_3$, Bismuthic Chloride. |
| Phosphoryl.....PO | | $(\text{PO})''' \text{Cl}_3$, Phosphoric Oxychloride. |

(4.) Tetratomic radicles, which replace 4 atoms of hydrogen :

| | | |
|--------------|--|--|
| Carbon.....C | | H_4C^{iv} , Marsh-gas. |
| Tin.....Sn | | $\text{Sn}^{iv} \text{Cl}_4$, Stannic Chloride. |

418. So far all is very simple, and if the radicles always exhibited the same atomicity, there would be little more to be said on the subject. But, with the exception of many of the monatomic class, radicles exhibit varying degrees of atomicity in different compounds. The series of nitrogen oxides afford an illustration of this. From their formulæ, N_2O , N_2O_2 , N_2O_3 , N_2O_4 , N_2O_5 , we observe that nitrogen might be placed in any class from monatomic to pentatomic, according to the oxide we select. Again, from the formulæ of the two compounds which tin forms with chlorine—namely, SnCl_2 and SnCl_4 , we should be in doubt whether to place tin in the diatomic or the tetratomic class.

419. This is a point of some difficulty, and should teach the student not to place too great reliance on the representations of atomic structure which are put forward by chemists. There are, however, several considerations in favour of the theory of definite atomicity.

(1.) There is a large class of radicles—for example, hydrogen, chlorine, &c., which have a perfectly well defined atomicity which they never lose. The existence of such a class tells in favour of the theory.

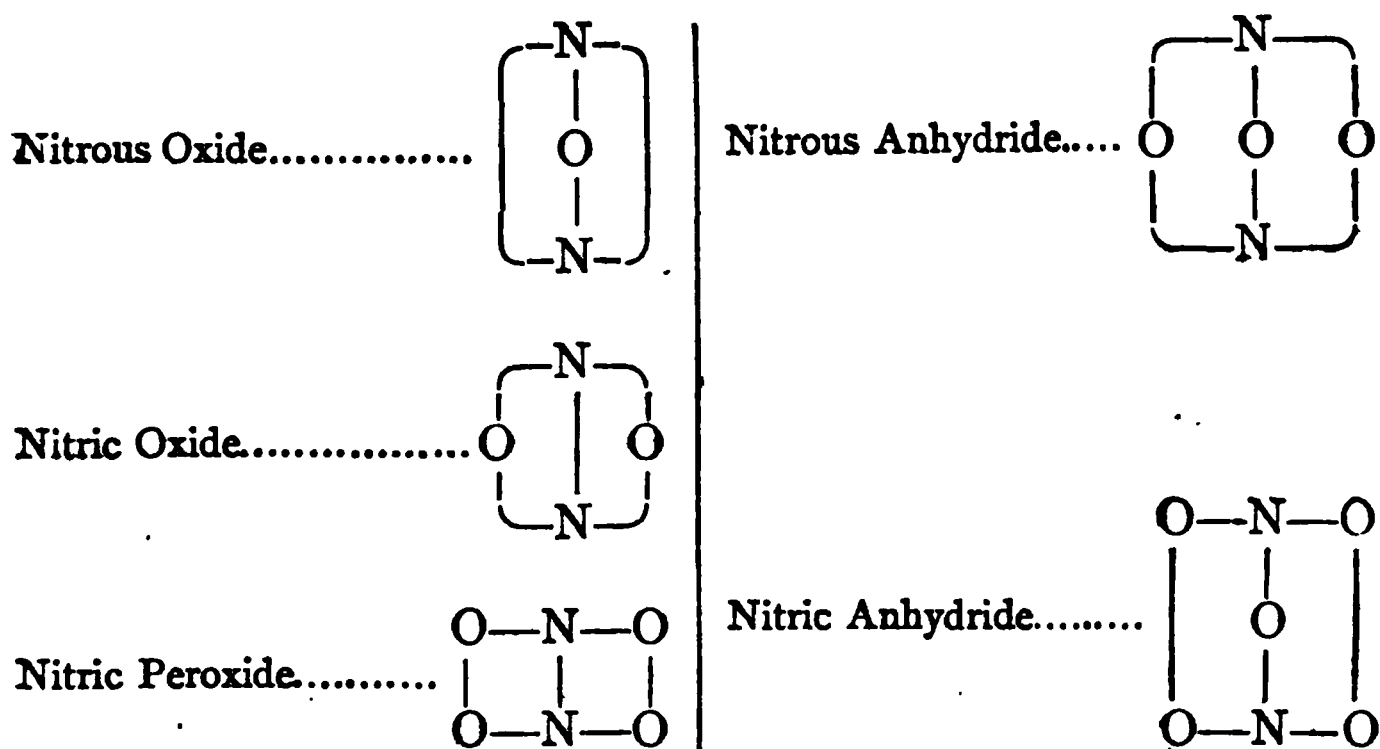
(2.) It is noticeable that every radicle shews a predominant atomicity—that is, forms one series of compounds more stable than the rest. Thus, of the two compounds of chlorine with tin, that which contains least chlorine, SnCl_2 , has a great tendency to take up more chlorine, and pass into the other compound, SnCl_4 . Cuprous oxide, Cu_2O , readily takes up oxygen to form cupric oxide, CuO . Hence, chemists consider themselves justified in referring such substances to the class indicated by the constitution of their most stable compounds: tin to the tetratomic, copper to the diatomic class.

420. An ingenious hypothesis has been started to account for variations in atomicity. It is supposed that every substance has a perfectly definite invariable atomicity, and that, in compounds which do not indicate this, its affinity is partly satisfied by combination with another atom of itself, just as has been mentioned in reference to the molecule. We may roughly illustrate this by the following comparison. Take a common bar magnet, and attach a piece of iron to each pole. Then it may represent a diatomic radicle combined with two atoms of a monatomic radicle—oxygen, for instance, combined with hydrogen in the molecule of water. Now, bring a similar magnet near the first, and place two dissimilar poles in contact, so that the combination forms a V. Then we have only two free points of attractive force, to each of which a piece of iron may be attached. The whole will now represent the compound formed by the union of two atoms of oxygen with two atoms of hydrogen, called hydric peroxide, H_2O_2 , in which part of the combining affinity of the oxygen is neutralised by combination with itself.

421. By a development of this view, it is possible to account for almost all variations of atomicity; we have only to consider that varying amounts of combining affinity are neutralised by self-saturation.* If we represent the directions of chemical

* This does not, however, account for the existence of such a compound as carbonic oxide, represented by the formula CO .

force by lines, the constitution of the nitrogen oxides may be thus shewn :



422. It cannot be too carefully remembered that the above are pure speculative hypotheses, and that new discoveries may make the present 'graphic,' or 'glyptic,' formulæ of little more value than the 'epicycles' of Ptolemy are to modern astronomy. The primary duty of the student of chemistry is to familiarise himself with the facts of the science, to observe minutely the conditions of a chemical change, and the proportions by weight and volume in which it takes place. This is nearly all that an elementary text-book like the present aims at teaching. It may introduce the learner to a few of the more important points of chemical theory, but proper justice to them can only be done by a reference to original memoirs, such as are found in the *Journal of the Chemical Society*, and Watts' *Chemical Dictionary*, and these the more advanced student should lose no opportunity of consulting.

CHAPTER XV.

INORGANIC CHEMISTRY—THE NON-METALLIC ELEMENTS.

423. The discussion of the laws of chemistry is followed by a consideration of each of the more important elements in turn, and of its chief compounds.

424. The latter are arranged in two great divisions—that, namely, of organic, and that of inorganic chemistry.

425. Organic chemistry may in the meanwhile be defined to be the chemistry of plants and animals, and of the substances directly and indirectly derived from them.

426. Inorganic chemistry is best defined negatively, as that section of the science which considers the properties of those substances which are not solely of vegetable or animal origin.

427. We commence with inorganic chemistry, in connection with the discussion of the elements.

Section I.—Oxygen, Hydrogen, Water.

OXYGEN.

| | Symbol. | Weight. | |
|---------------|----------------|---------|--|
| Atom..... | O | 16 | 1 litre weighs 1.430 gm. Density (air = 1.000) = 1.105. |
| Molecule..... | O ₂ | 32 | |

428. At all observed temperatures, oxygen, when uncombined, is a gas. It is the most widely diffused body in nature, forming

one-fifth part of atmospheric air by volume, and eight-ninths of water by weight, besides being a constituent of nearly all the earths and rocks of the globe. It is estimated to form nearly one-half of our planet, and more than one-half of living plants and animals.

429. Its name is derived from the Greek $\acute{\alpha}\nu\alpha\varsigma$ (oxys), acid, and $\gamma\epsilon\gamma\alpha\omega$ (gennao), I call into being, or give rise to—in allusion to its property of forming acids, by combining with other elementary bodies. The word oxygen thus signifies the *acid-producer*, and was given to this element at a time when all acids were believed to contain oxygen, and to owe their acidity to its presence. We now know many acids, such as hydrochloric, which contain no oxygen, and we do not impute the acidity of those which possess it, to its occurrence in them. We retain the name, therefore, simply as a convenient appellation for this important substance.

430. *Preparation.*—Oxygen is generally obtained by the application of heat to some oxide or salt containing it. An experiment has been already given (par. 13), which shews the mode of obtaining it from mercuric oxide. This method of preparing oxygen is never practised in the laboratory, in consequence of the costliness of the oxide of mercury, when used in considerable quantity; but it deserves the student's special attention, owing to the simplicity of the decomposition which leads to the evolution of the gas, and because it is the first substance from which oxygen was obtained—namely, in 1774, by Dr Priestley.

431. The salt most suitable for the preparation of oxygen is potassic chlorate, a substance largely consumed in the arts, and therefore easily procured.

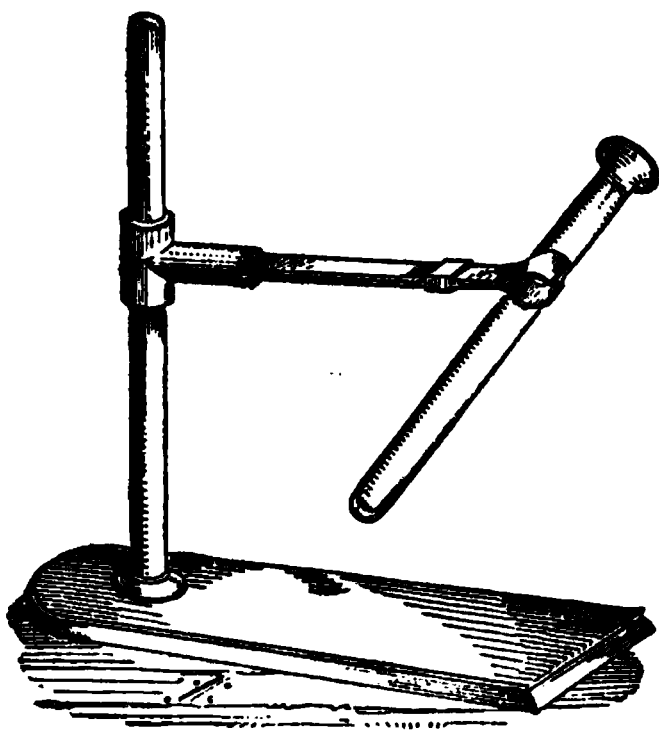


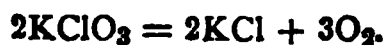
Fig. 28.

To prepare oxygen from it, a few crystals may be placed at the bottom of a test-tube (fig. 28), and the flame of a spirit-lamp applied. The salt quickly melts, and becomes, although quite free from water, a clear liquid. It then begins to effervesce, in consequence of the rising through it of multitudes of bubbles of oxygen, and this effervescence continues till the whole of the gas which the salt contains has been disengaged.* If a red-hot match be plunged into the tube whilst the melted potassic chlorate is effervescing briskly, it will burst into full flame, and burn much more brilliantly than it does in air.

432. When oxygen is required in large quantity, a retort is substituted for the test-tube, and the gas is collected in jars at the pneumatic trough. The potassic chlorate is employed as the source of the oxygen, but it is previously mixed with from one-third to one-fifth of its weight of manganic oxide (black oxide of manganese), or red oxide of iron, which have a remarkable power of increasing (in a way not easily explained) the rapidity with which potassic chlorate evolves oxygen, although these oxides are found at the end of the action entirely unchanged, and may be used over and over again.

433. The pneumatic trough referred to above is a box made of wood or tin plate, generally about 40 cm. long, 30 cm. in breadth, and 25 cm. in depth; but it may be made of any size. At one side, parallel to the length of the trough, a shelf, A (fig. 29), is fixed, about 7 or 8 cm. below the edge of the box. Holes are bored in this shelf at short distances, in order to allow gas to be passed into jars, standing on it with their mouths over the apertures. A movable stool, B, stands within the trough, of such breadth as nearly to fill the space between the free edge of the shelf at the one side and the wall of the trough on the other, and of such height, that its upper surface is exactly on a

* The action is expressed by the following equation:



The significance of this mode of expression is explained in Chap. XII., par. 353; but the beginner is not advised to read that chapter until this and the two following sections have been studied.

level with that of the shelf. This stool has an aperture in the centre of its upper surface, which forms the termination of a funnel-shaped cavity hollowed out in the wood, so that its wider mouth looks downwards, and the aperture already referred to corresponds to the end of the pipe of the funnel, and points

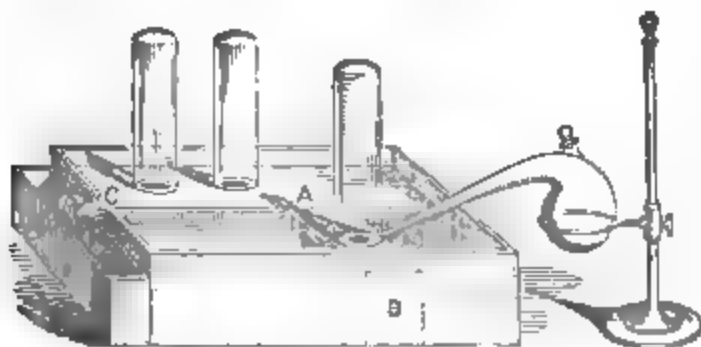


Fig. 29.

upwards. A spout, C, projects from one extremity of the trough, about 5 cm. above the level of the shelf. It serves to carry off the excess of water discharged from the jars as they are filled with gas. A smaller trough is placed permanently to receive the water which runs off. Such an arrangement is rendered necessary by the fact, that at the beginning of any process for collecting gas at the pneumatic trough, all or the greater number of the jars which are to be filled with the elastic fluid must be arranged full of water on the shelf, whilst at the end of the process the whole of the jars are emptied of water, and the trough which receives it would run over, if the spout and smaller reservoir were not provided for its reception.

434. In using the pneumatic trough, water is poured in till it reaches the level of the spout, and begins to flow over; it should then stand some 4 cm. above the level of the shelf and stool. The jars in which the gas is to be collected are filled with water by plunging them obliquely with their closed ends downwards into the cavity, or, as it is called, the well of the trough. When full of water, they are inverted, so as to have their open mouths downwards, and are lifted, or rather slid, on to the shelf, where they stand till each in its turn is about to

be filled with gas (fig. 30). If so much water be removed from the well of the trough in filling the jars that it sinks to the level

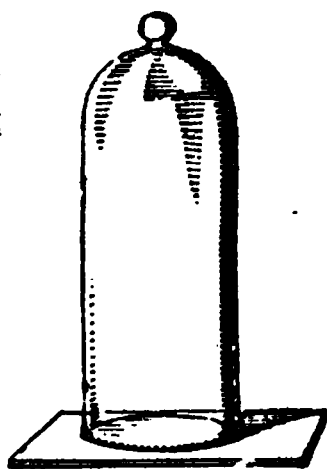


Fig. 30.

of the shelf, then the trough must be replenished with water; for the jars cannot be kept full of liquid unless their mouths are below the surface of the liquid, and a column more than 2 cm. in height should be left above the shelf. If this be neglected, in the rapid transference of jars to and from the shelf, air will certainly be allowed to enter, and the collection of gas arrested till the jar is filled with water anew.

435. The further use of the trough will be best illustrated by continuing the description of the preparation of oxygen. Thirty grammes of potassic chlorate, and seven grammes of manganic dioxide, should be weighed out, powdered (if necessary), and dried separately on the sand-bath. When dry and cool, they may be intimately mixed in the mortar, an equal bulk of fine dry sand being added, to make the evolution of gas more regular.* The mixture having been placed in a retort (fig. 31), the stopper is to be tightly fixed in, and

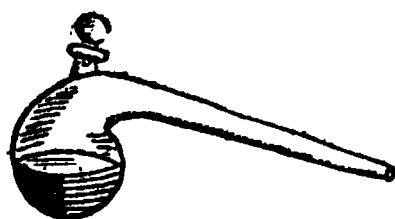


Fig. 31.



Fig. 32.

the beak or extremity of the long tube of the retort plunged below the surface of the water in the trough. Instead of a retort, a flask (fig. 32) may be used, furnished with a bent tube, passed through a cork, which fits the neck of the flask.

* This addition of sand should on no account be omitted; otherwise there will almost certainly be a tumultuous rush of gas.

The movable stool is then pushed along till it stands over the beak of the retort. Heat is now applied to the retort or flask by means of a spirit-lamp or a gas flame, the retort or flask being supported in one of the rings of a retort-stand (fig. 33). The first effect of the application of heat is to expand and expel the air in the retort, which comes bubbling up through the aperture in the stool, and is allowed to escape. When the pure gas succeeds it, one of the jars full of water standing on the shelf is transferred from it to the stool, its mouth being kept under water during the transference. The gas now rises into the jar, causing the water to descend till it has expelled the whole of it. The jar, when filled, is slid back again to the shelf, and another full of water removed to the stool, and this manipulation is repeated till all the jars are filled with gas, or the latter ceases to be evolved.

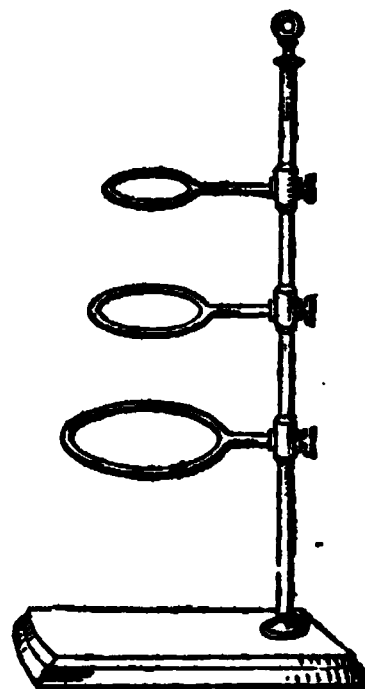


Fig. 33.

436. 122.5 grms. of potassic chlorate contain 35.5 grms. of chlorine, 39 grms. of potassium, and 48 grms. of oxygen. When it is heated, the whole of the oxygen is evolved, and the chlorine and potassium remain in combination, forming a white salt, potassic chloride, resembling in appearance and many properties the corresponding sodic chloride (common salt). From these facts we can easily calculate the amount of oxygen obtainable from a given weight of the salt, by a simple proportion sum. Thus, taking 30 grms.,

$$122.5 : 30 :: 48 : 11.75 \text{ grms.}$$

which is the weight of oxygen obtained. And, since 1.43 gm. of the gas measures 1 litre (at standard pressure and temperature, par. 373), 11.75 grms. will measure ($\frac{11.75}{1.43} =$) 8.21 litres.

437. When the contents of a jar are to be examined, it is removed altogether from the trough, by sliding it off the shelf on to a gas-tray, as it is called. This consists of japanned tin

plate, or sheet-zinc, and exactly corresponds in shape to the cover of a cylindrical canister or the lid of a round snuff-box. This tray is filled with water, and the jar, with its mouth down, being transferred to it, the two are lifted off together, the tray being held in one hand, and the other laid on the closed end of the jar to keep it from falling over. A jar of gas may be kept apart for any length of time, provided only the tray be kept full of water. If the mouths of the jars are ground, squares or disks of plate-glass which fit air-tight will be found still more convenient than the gas-trays.

438. When the gas is to be examined, as, for example, by plunging a lighted candle into it, the jar is quickly inverted, and the tray lifted off. In doing this, the jar should be held above the pneumatic trough, so as to allow the water which runs out of the tray to be received by it, and prevent it wetting surrounding objects.

439. Other gases are collected at the pneumatic trough in the same way as oxygen. If, however, a gas be very soluble in water, that liquid must be dispensed with, and mercury employed in its place. We accordingly distinguish two varieties of the pneumatic trough—the water and mer-

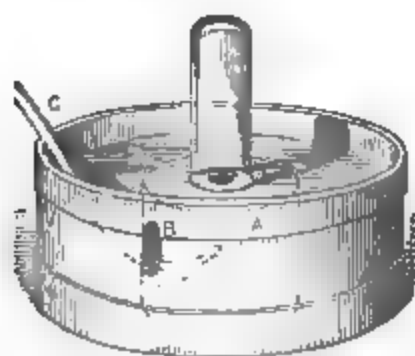


Fig. 34

curial. Troughs are also constructed of stoneware, and have the advantage of being cleanly and water-tight. The accompanying figure (fig. 34) represents one, with a stoneware stand, A, for the jars, which has a lateral aperture, B, for the beak of the retort or tube, C, delivering the gas. A tub, a wash-hand basin, a foot-pail, a leaden cistern or sink, or any other water-

tight box, may be used as a pneumatic trough, with a couple of bricks or flat stones to support the jars.

440. Besides the pneumatic trough, with its glass jars, it is desirable to have vessels of larger capacity, in which considerable quantities of gas can be collected, and from which it can

be drawn off at pleasure. Such vessels are called gas-holders or gasometers, and are constructed of tin plate, or, better, of zinc or copper. The figure (fig. 35) represents one of the most convenient, distinguished by its inventor's name, as Pepys' gas-holder. A is a metallic drum or cylinder; B, a cistern, communicating with A by a small tube C, which terminates in the roof of the cylinder, and a large one, D, which descends to nearly the bottom; E is a pillar of support to the cistern; F is a tube placed at an angle with the cylinder, and provided with a cover which screws into its mouth, and fits it air-tight; G is a stop-cock, projecting laterally from the top of the cylinder.

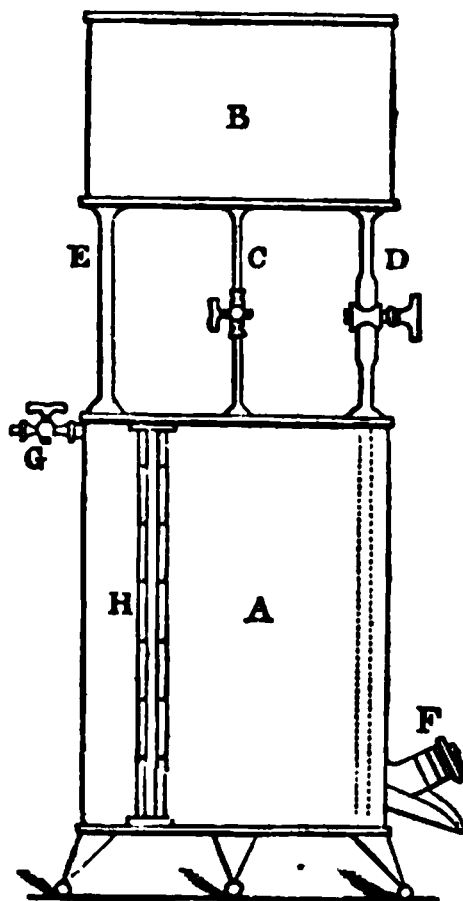


Fig. 35.

441. In the figure the gas-holder is represented in the condition in which it would ordinarily be called empty—in other words, full of air. As a preliminary step to filling it with gas, water is poured into the cistern B. It descends by the tube D, and partly by C, whilst the air escapes by C and G. When the water runs out at G, the cylinder is full, and all the stop-cocks are shut. The cover of the oblique tube F is then unscrewed, and the beak of the retort, or exit tube of the flask, from which the gas is issuing, is inserted through F, and pushed in till its end is fairly within the cylinder. The gas rising vertically, accumulates in A, whilst the water it displaces flows out at F, past the neck of the retort or tube of the flask. When the water is all expelled, the retort or flask is withdrawn, and F closed again with the cap. A glass tube or gauge, H, communicating at each end with the cylinder, and in which the water stands at the same level as in A, allows the amount of gas in the latter to be readily observed.

442. The gas is drawn off either by C or by G. If a jar is

to be filled, water is poured into B, and the jar full of water is

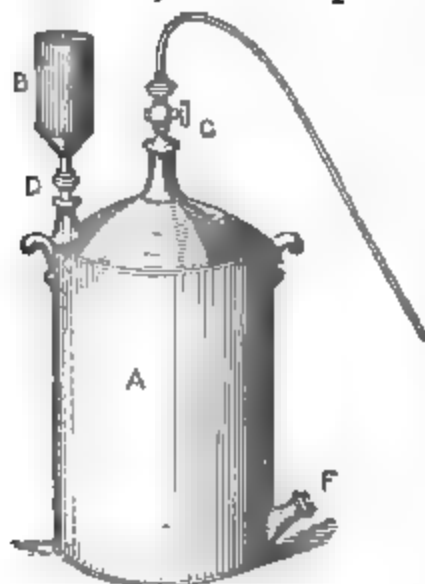


Fig. 36.

placed mouth downwards over C. C and D are then opened, and the water which descends by D expels the gas by C. If a current of gas is wished, as for the lime-ball light or the oxy-hydrogen blowpipe, the tube to convey it is attached to the end of G. B is kept full of water, and when D and G are opened, the gas rushes out by the latter. The stop-cocks at D and G admit of the current being very nicely regulated.

443. Fig. 36 represents another and cheaper gas-holder, made of stoneware. Its construction is, in essential points, similar to the one described above, and the letters refer to the corresponding parts of fig. 35. Another convenient receptacle for gases is a bag made of stout india-rubber cloth. This, from its portability, is often used to hold a supply of oxygen for the lime-light; but owing to the porosity of india-rubber, the gas cannot be kept pure in such bags for any length of time.

444. The process above described is that by which oxygen is generally made for laboratory purposes; but several other processes for obtaining the gas may be mentioned.

(1.) When manganic oxide is heated to redness in an iron bottle, or a piece of iron gas-pipe closed at one end, it gives off one-third of the oxygen it contains,* and as the substance is very cheap, this method is sometimes used, when large quantities of oxygen are required.

(2.) We have already seen that oxygen may be obtained by the electrolysis of water. It may also be obtained by the action of chlorine on water. Chlorine has a great affinity for hydrogen, and when it is mixed with steam, and passed through a red-hot

* $3\text{MnO}_2 = \text{Mn}_2\text{O}_3 + \text{O}_2$

porcelain tube, hydric chloride is formed, and oxygen is set free.* The gas may be collected over the pneumatic trough, the hydric chloride being absorbed by the water.

(3.) Other modes of obtaining oxygen will be referred to under the heads of HYPOCHLORITES and BARIUM.

445. *Properties.*—Oxygen has no colour, odour, or taste. It is heavier than air, in the proportion of about 11 to 10. It cannot be liquefied or solidified when uncombined. It is soluble in water to the extent of 30 c.c. of the gas in 1 litre of water. This is, comparatively speaking, a slight solubility; nevertheless, it is a property of oxygen of great importance in relation to plants, but still more to water-animals, the greater number of which are dependent on this dissolved oxygen for the support of respiration and life. Fishes die at once if placed in water which contains no oxygen in solution. The sea and other natural beds of water are constantly dissolving this gas from the atmosphere above them.

446. The most striking property of oxygen is its power of supporting and enlivening combustion. In illustration of this, the following experiments may be tried:

447. 1st, Kindle a match of wood, and blow it out, leaving the end red-hot. Plunge it into a jar of oxygen, when it will burst into bright flame. Withdraw it immediately, blow it out, and introduce it a second time into the gas: it will be kindled afresh; and if the gas be pure, a splinter of wood may be blown out and rekindled twelve, fourteen, or twenty times, according to the size of the jar. A wax or tallow candle will exhibit the same phenomenon, but it is difficult, in extinguishing a wax-light, to retain the wick red-hot.

448. 2d, Place a piece of roll sulphur in a small tin cup, on a pedestal standing on a plate, or in a cup like that used in the next experiment, and set it on fire by touching it with a red-hot wire. When it has begun to burn, plunge it into a pretty large jar or globe of



Fig. 37.

* $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$.

oxygen. The sulphur immediately bursts into fuller combustion, burning with a rich, purple-blue flame, and evolving a much intenser heat than when burned in common air.

449. *3d*, Dry carefully a piece of phosphorus about the size of a split pea. It is to be deprived of adhering moisture by gently pressing it between folds of blotting-paper, friction being as much as possible avoided, as it may kindle the phosphorus, and occasion a severe burn to the experimenter. The phos-

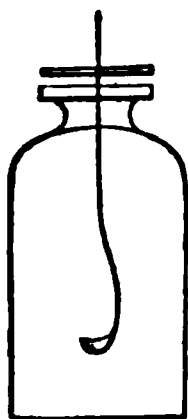


Fig. 38.

phorus is then to be placed in a small metallic cup attached to a wire (fig. 37), and after it has been inflamed by touching it with a hot wire, it is to be introduced into a glass globe, or other convenient jar, filled with oxygen (fig. 38). It burns with a brilliancy so intense that the eye cannot bear it. The heat evolved is also very great, and frequently occasions fracture of the vessel in which the experiment is made. To guard against this, care should be taken that the phosphorus is dry, otherwise it spirts, and portions of it, in a state of combustion, are projected against the sides of the vessel, and occasion its destruction. Some water should always be left, or placed at the bottom of the glass vessel, to receive any phosphorus which may boil over, and the vessel itself should be of considerable dimensions, so that the burning combustible may be at some distance from its sides. An experiment similar to that recorded above may be made with wood-charcoal, a fragment of which, after being well kindled, is to be suspended by a wire in a jar of oxygen. A charred cork burns in these circumstances very prettily.

450. *4th*, The most brilliant of all the experiments on combustion in oxygen is that with iron wire. For its performance a glass vessel is needed resembling a large stoppered bottle without a bottom. A stopper is placed in the neck of this 'deflagrating' jar, and it is filled at the pneumatic trough with oxygen in the usual manner, and removed from it on a gas-tray. A bundle of the thinnest iron wire, such as is sold under the name of harpsichord wire, is formed into a spiral, as large in

diameter as the neck of the jar will allow to enter easily. This is done by coiling the wire round a cylinder of the proper dimensions. A piece of very fine watch-spring, which can be obtained from any watchmaker, may be used instead of the iron wire. It may be softened by heating it to redness in the flame of a lamp, and allowing it to cool slowly. One end of the spiral is tipped with brimstone, by heating it, and immersing it in flowers of sulphur till a small portion of the latter adheres to it. The other end of the spiral is fixed into a cork, which fits the neck of the bottomless jar. The sulphur having been kindled, the stopper of the jar is quickly withdrawn, and the spiral inserted, the cork to which it is fixed being firmly pressed down, so as to close the mouth of the jar. The sulphur bursts into full flame, and kindles the iron, which in its turn burns with great brilliancy, evolving a bright light, and letting white-hot drops of fused oxide of iron fall from it as it burns away. This and the other experiments on combustion described, are seen to greatest advantage when performed in a dark room.



Fig. 39.

451. Combustion in oxygen and in atmospheric air is essentially the same phenomenon—air consisting of oxygen diluted by four times its volume of the inactive gas nitrogen. Combustion, however, as might be expected, is much slower, and less brilliant, in atmospheric air, one-fifth part of which only is oxygen. Otherwise, the phenomena presented by bodies burning in air, and in oxygen, differ only in degree, and not in kind. A combustible gives out an intenser heat and light in the pure gas than in the diluted one, but it evolves the same *quantity*, at least of heat, in both cases—that is, the same weight of ice will be melted during the combustion of 12 grms. of charcoal with 32 grms. of oxygen, whether the oxygen be supplied pure, or be furnished in the state of dilution in which it occurs in atmospheric air. In the first case, however, the charcoal will burn a great deal more rapidly, and in so

doing will produce a much higher temperature than when burning more slowly in air. The quantity of heat evolved will be exactly the same; for, although the charcoal burned in oxygen will melt ice much more rapidly than the charcoal burned in air, the former will not melt a greater weight of ice than the latter.

452. During combustion, an oxide of the combustible is invariably formed. Thus the iron wire in the last experiment unites with the oxygen to form the black or magnetic oxide of iron, Fe_3O_4 . Phosphorus forms phosphoric anhydride, P_2O_5 . Sulphur produces, by combustion with the oxygen, sulphurous anhydride, SO_2 . Charcoal forms carbonic dioxide, CO_2 . A match or candle contains two combustibles—carbon and hydrogen; the former is oxidised into carbonic dioxide, the latter into water.

453. We are unable to explain the cause of the evolution of heat and light which accompanies oxidation. In the great majority of cases where chemical combination occurs, heat and light are evolved, whether oxygen be one of the combining bodies or not; so that production of a high temperature, and the development of light, appear to accompany all cases of intense chemical combination. There is nothing, therefore, peculiar, so far as theory is concerned, in the combustion of bodies in oxygen; but as it is the substance by means of which we burn the fuel occurring at the earth's surface, and thereby provide ourselves at will with artificial heat and light, the relation of oxygen to combustion is more important than that of any other body.

454. Substances which, by combination with the marked combustibles—such as charcoal, sulphur, phosphorus, and the metals—cause the evolution of heat and light, are called *supporters of combustion*. Thus, in our ordinary fireplaces, carbon and hydrogen are the combustibles, and the oxygen of atmospheric air supports their combustion.

455. The compounds of oxygen are divided into three classes: 1st, *Neutral oxides*—such as water, H_2O ; carbonic

oxide, CO ; nitrous oxide, N_2O —which do not possess a sour taste; do not change the tints of colouring matters; and do not combine with acids, or with bases to form salts. The student can verify those properties with water. *2d, Acid oxides*, which combine with water to form substances which have a sour taste; change vegetable blues to red, and vegetable browns to yellow; and form salts by combining with bases. To observe those properties, a little water may be shaken up in the jar in which the sulphur or the phosphorus was burned (par. 450), and the liquid, which is a solution of hydric sulphite or phosphate, may be examined. To make manifest its action on colouring matter, an infusion must be made of the purple cabbage, or of the colouring matter *litmus*, which can easily be procured from any druggist. The purple-blue liquids so prepared are at once changed to red by a very small addition of the acids referred to. Solutions of brown colouring matter are prepared by pouring hot water on powdered turmeric, or medicinal rhubarb, and adding to the yellow liquid so procured a little sodic carbonate, which renders it brown. The acid will then change it back to yellow. To observe the third character, soda, one of the most powerful bases, may be added to dilute hydric sulphate, or potass to dilute hydric nitrate, till, in either case, the liquid has no longer a sour taste, and does not turn blue litmus red. The liquid is then to be gently evaporated, and crystals of Glauber's salt, sodic sulphate, in the one case, of saltpetre, potassic nitrate, in the other, will be procured. *3d, Basic oxides*, which in the best marked examples have a soapy taste, as seen in potass and soda; change vegetable reds to blue or to green, and yellows to brown, exactly reversing the effects of acids; and form salts by combining with acids. Only a few of the bases have a taste, or action upon colouring matter; all of them, however, possess the third character. Their action on colouring matter may be observed by adding a solution of potass, soda, or lime-water to an acidified, and therefore red, infusion of cabbage or litmus; when its colour changes to green in the first case, and to blue in the second. If these

basic oxides are added to infusion of turmeric or rhubarb, it is at once changed from yellow to brown.*

456. *Ozone*.—It has long been known that when a stream of electric sparks is passed through a tube containing oxygen, the gas acquired some new properties. This has been referred to already (page 100), and the method was there indicated of producing the greatest effect, namely, by employing, not the actual spark-discharge, but the 'silent discharge.' The apparatus employed by Siemens consists of two tubes, the one so much smaller in diameter than the other, that, when placed inside it, a small space is left between the two. The inside of the inner tube and the outside of the outer tube are coated with tin-foil, and connected respectively with the poles of an induction coil. When perfectly pure, dry oxygen is passed through the space between the tubes while the coil is in action, the issuing gas is observed to be modified, as follows :

457. (1.) It has acquired a strong oppressive odour, the same which is observed in the air near an electrical machine in action.

(2.) It corrodes india-rubber and many other substances almost immediately. Hence no india-rubber tubing can be used in the above apparatus.

(3.) When passed into solution of potassic iodide, iodine is liberated, as may be shewn by the addition of a little starch, when the characteristic deep blue compound will be formed (see under the head of IODINE).

(4.) When brought into contact with mercury, silver, and many other metals, an oxide of the substance is formed. It also bleaches many colouring matters, such as indigo.

(5.) When the gas is passed through a tube, heated to about 250° , all the above properties disappear, and nothing but ordinary oxygen issues from the end of the tube.

* Several of the acid oxides, such as silicic anhydride, SiO_2 , and the majority of the basic oxides, as ferric oxide, Fe_2O_3 , are tasteless, and without action on colouring matter. The only essential character of an acid oxide is, that it neutralises a basic oxide, and of a basic oxide, that it neutralises an acid oxide, so as to form a salt.

458. It is found that oxygen, after being exposed to the action of electricity, has contracted in volume, more or less; the utmost contraction hitherto obtained being about $\frac{1}{12}$ th of the original bulk. The gas, when heated to 250° , recovers its original volume. Another remarkable fact is, that the gas, after being caused to act upon many (though not all) substances, is absolutely unaltered in volume. Thus, if 10 c.c. of the altered gas is brought into contact with mercury, the metal is oxidised, but 10 c.c. of oxygen remain after the action.

459. These phenomena are explained by supposing that a substance is formed, called ozone (Gr. $\sigma\zeta\omega\nu$, smelling), from its characteristic smell, the molecule of which consists of three oxygen atoms (the molecule of ordinary oxygen consisting of two oxygen atoms*). This third atom is retained in the molecule by a feeble force, and hence arise the intense oxidising powers of the substance. When this atom is withdrawn, a molecule of ordinary oxygen remains, and hence there is no contraction in bulk.†

460. It is found impossible, with our present methods, to convert the whole of the oxygen into ozone, unless the latter is withdrawn as fast as it is formed. After a certain point of concentration, so to speak, the ozone, probably from the heat of the discharge, is re-converted into ordinary oxygen, as soon as produced. By keeping the whole apparatus at or below the freezing-point, the production of ozone may be greatly increased.

461. Ozone may be formed in many other ways. The oxygen obtained from the electrolysis of water always contains it, and it is produced in many processes of oxidation. A simple method of obtaining it is to place a stick of phosphorus in a bottle filled with air, and having a little water at the

* Thus, if we represent the molecule of oxygen by O_2 , the molecule of ozone will be O_3 , both molecules, of course, occupying the same space.

† An analogous case is presented by carbonic dioxide. When a given volume of the gas is passed over heated iron, the iron is oxidised, and the gas is reduced to carbonic oxide, but no change in volume occurs. The atom of oxygen is given up without altering the size of the molecule.

bottom to absorb the phosphoric oxide formed. After the lapse of a few minutes, sufficient ozone will be formed to be recognised by its smell and its action on a piece of white blotting-paper dipped in a solution of potassic iodide, to which a little fresh starch solution has been added. The presence of ozone in the atmosphere will be alluded to shortly (par. 505).

HYDROGEN.

| | Symbol. | Weight. | |
|---------------|----------------|---------|---------------------------|
| Atom..... | H | 1 | 1 litre weighs 0.0896 gm. |
| Molecule..... | H ₂ | 2 | Density = 0.0693. |

462. Hydrogen does not appear to exist uncombined on the earth; but meteorites have been shewn to contain considerable quantities of it imprisoned in their pores; and spectrum analysis (page 81) proves that it is present in the sun's atmosphere, Fraunhofer's lines C, F, and G, being due to absorption by hydrogen. It is one of the elements of water, and is a constituent of all plants and animals, and of the great majority of the substances derived from them.

463. *Name.*—Its name is derived from ὕδωρ (hydor), 'water,' and γίνομαι, 'I generate,' so that it signifies the 'water-producer.'

464. *Preparation.*—The simplest mode of preparing hydrogen is by sending a galvanic current through water, when it suffers resolution into its two constituent gases, which may be collected separately.

465. Another method—interesting from the simplicity of the change which occurs, but much too costly to be employed in practice on the large scale—is to fold up a fragment, about the size of a pea, of the metal sodium in blotting-paper, and pass it rapidly under the edge of a gas-jar standing full of water on the shelf of the pneumatic trough. The sodium, which is lighter than water, ascends within the jar; and as soon as the paper becomes soaked, decomposes the water with great rapidity.

This metal has a greater affinity for oxygen than hydrogen has. It is able, accordingly, to decompose water by uniting with its oxygen, and letting its hydrogen go free. The latter gas collects at the upper end of the gas-jar, whilst the oxygen, together with half the hydrogen, remains in combination with the sodium, forming sodic hydrate or caustic soda.* If the jar be filled at the beginning of the experiment with infusion of purple cabbage instead of pure water, the presence of sodic hydrate will be rendered manifest by the liquid changing in colour from purple to green.

466. Iron cannot decompose water at ordinary temperatures, but if heated red-hot, it acts like sodium; with this difference, however, that all the hydrogen is evolved from water, none remaining in combination with the metal.† This property of iron is generally illustrated by sending steam through an iron tube like a gun-barrel, placed across a small furnace, when the iron unites with the oxygen of the water (steam), and the hydrogen is set free; but so complicated and troublesome an apparatus is not necessary for the purpose. If a bar of iron be raised to a full red heat, it will be found to decompose water when plunged below its surface. To prove this, all that is needed is to thrust the red-hot bar below the mouth of a gas-jar filled with water, when bubbles, apparently of air, will be seen to rise from the iron, and collect in the upper end of the jar. These bubbles consist of hydrogen gas mixed with a little air.

467. The above methods of obtaining hydrogen are of more theoretical than practical value. The gas is usually prepared by the action of zinc or iron upon hydric sulphate (sulphuric acid). Zinc is preferred to iron on account of its greater purity; and it is usually 'granulated,' or reduced to small fragments by being melted in a ladle, and poured in a fine stream into



cold water. About 30 grms. of this granulated zinc should be placed in a flask or bottle, fitted with a cork pierced with two holes, one to receive a bent delivery-tube, the other a long tube-funnel. The end of the latter should reach nearly to the bottom of the flask. The flask may be supported in a retort-stand, as shewn in fig. 40, the end of the delivery-tube dipping

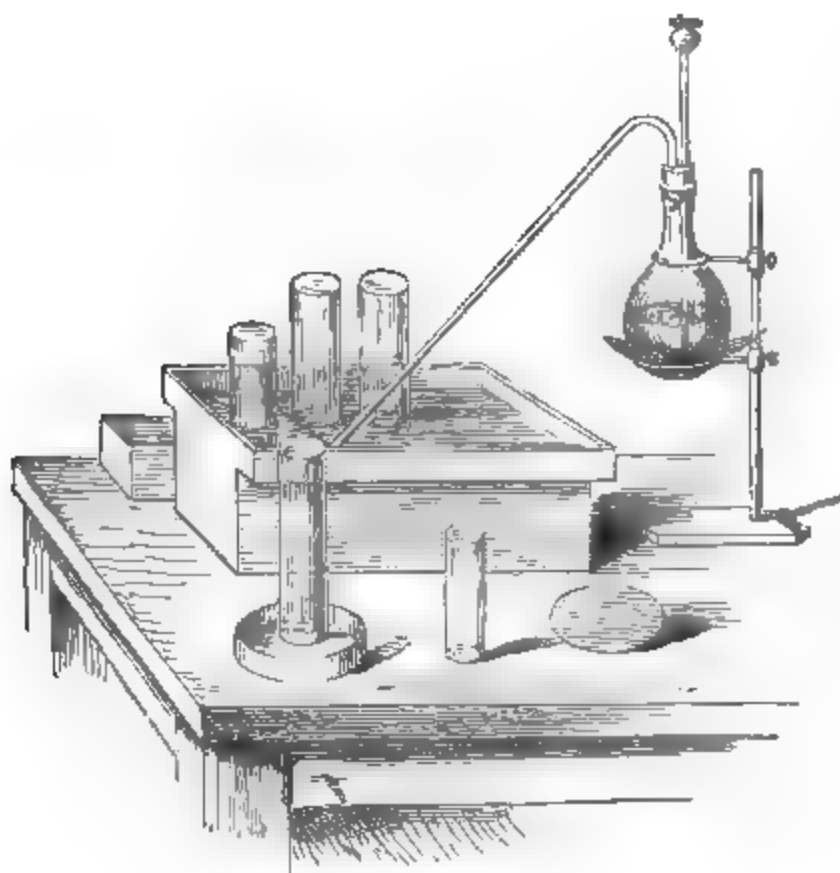


Fig. 40.

under the shelf of the pneumatic trough. Enough water may now be poured down the funnel to fill the flask about one-fourth; and then, on pouring in 20 or 30 drops of strong hydric sulphate, hydrogen gas will be almost immediately evolved with effervescence. Care must be taken not to add too much acid at first, lest the action should become too violent: it must be added in successive small portions, just sufficient to keep up a regular stream of gas. Since, as will be seen, hydrogen forms

an explosive mixture with air, no lighted lamp should be near the apparatus at first; and the first two jars collected (or twice the volume of the flask) must be thrown away, as they will contain hydrogen mixed with the air in the flask.

468. The nature of the action is similar to that in the other methods mentioned: 98 grms. of hydric sulphate contain:

| | |
|---------------|---------|
| Hydrogen..... | 2 grms. |
| Sulphur..... | 32 " |
| Oxygen..... | 64 " |
| | 98 " |

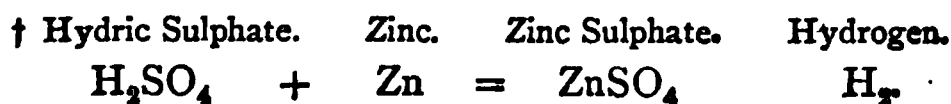
When zinc is brought into contact with the acid, diluted with water,* the 2 grms. of hydrogen are replaced by 65 grms. of the metal, a salt, called zinc sulphate, being formed, while the hydrogen is given off.† Knowing, then, that 2 grms. of hydrogen are obtained for every 65 grms. of zinc dissolved, we can easily calculate the amount obtainable from the 30 grms. of zinc taken. Thus,

$$65 : 2 :: 30 : 0.92 \text{ gm.}$$

And since 0.0896 gm. of hydrogen measure 1 litre, 0.92 gm. will measure $(\frac{0.92}{0.0896} =)$ 10.26 litres.

469. *Properties.*—Hydrogen is the lightest body in nature, being fourteen and a half times lighter than air, and sixteen times lighter than oxygen. Its lightness may be demonstrated by filling a bladder, or waterproof-cloth bag, with hydrogen, and employing this, by attaching it to a tobacco-pipe, to blow soap bubbles with the gas. These ascend with great rapidity. A better method is to fill a small balloon with hydrogen, which can easily be done by fixing in the neck of a bottle containing zinc and diluted sulphuric acid a vertical tube, over which the mouth of the balloon, previously well compressed to empty it of air, is passed, and held till

* When the strong acid alone is used, sulphuric dioxide, not hydrogen, is obtained, owing to a secondary action.



it, and can be kept cool, to collect the water produced. For every gramme of hydrogen burned, nine grammes of water will be obtained.

474. If hydrogen, instead of being burned at a jet, or at the mouth of a jar, be mingled with air, or oxygen, before a light is applied, the combustion of the entire volume of inflammable gas is instantaneous (or nearly so), and is attended by a loud explosion. We have already referred several times (pages 11, 103) to this experiment, and it will be remembered that water was shewn to consist of two volumes of hydrogen combined with one of oxygen. These are the proportions, then, in which the gases must be mixed in order that the combustion may be complete, and no residue of either gas may be left. If we employ air, one-fifth of which only is oxygen, we must take five volumes to two of hydrogen, or two and a half of air to one of the gas. Wide-mouthed vessels much thicker and stronger than the ordinary gas-jars must be used in these experiments; and it is well to wrap the vessel in a towel before applying a light, so that, if the glass should break, the hands may escape injury. The fact that hydrogen forms an explosive mixture with air, should be kept in recollection whenever experiments are made

with the gas, as many accidents have occurred from ignorance or forgetfulness of the fact.

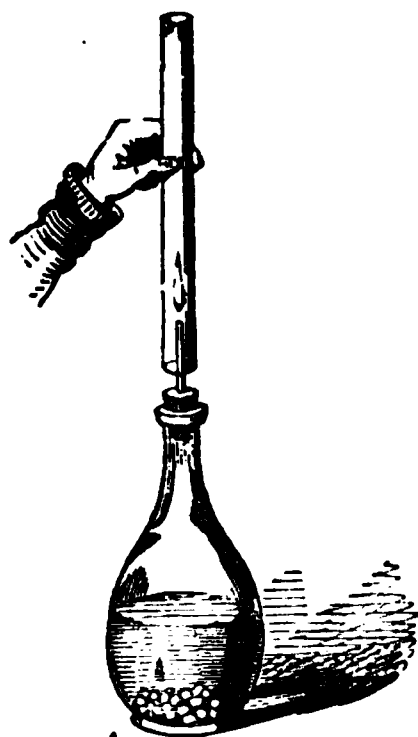


Fig. 43.

long, placed over it like a chimney (fig. 43). The flame

475. The sound in such explosions is occasioned by the concussion of the air, from the propulsion against it of the steam resulting from the combination of hydrogen and oxygen, which is in a highly expanded state, owing to the heat produced. If the detonations are made to succeed each other very rapidly, a musical note is produced. To observe this, a jet of hydrogen should be kindled, and a glass tube, open at each end, about 60 cm.

elongates, and begins to flicker, an effect which is owing to the tube preventing a large volume of air reaching the jet. The gas, in consequence, has to mix *comparatively* slowly with a volume of air sufficient to burn it, and combustion then happens with a slight detonation. This process of mixture with air, followed by explosion, proceeds with great rapidity, so that the detonations succeed each other with such swiftness as to prevent the ear observing the intervals between them. A continuous sound, or musical note, is thus produced, which varies according to the size of the jet, and the length and diameter of the glass chimney placed over it. This arrangement has been called the hydrogen harmonicon; but any of the combustible gases will produce musical notes if burned in the same way.

476. Hydrogen and oxygen may be preserved mixed for any length of time without combining. Combination is determined in a moment by the introduction of any body at a red heat, by the application of flame, or the passage of an electric spark. Another very interesting method of determining the union of the gases, is the introduction into a mixture of them of a piece of the metal platinum, perfectly clean; or, better, of a piece of spongy platinum (see under PLATINUM), held in a ring of platinum wire, which causes their rapid union, with the evolution of heat and light.

477. An instantaneous lamp has been devised, which takes advantage of this property of platinum. It consists essentially of a vessel in which hydrogen is generated and stored (fig. 44), with a stop-cock, *a*, by means of which a jet of the gas can be directed against some finely powdered, or, as it is called, spongy platinum, contained in a small brass cup, *b*. The hydrogen mingles with air before reaching the platinum, which at once inflames the mixture, and a match may be lighted at the flame. This ingenious apparatus is now superseded by the lucifer-match.

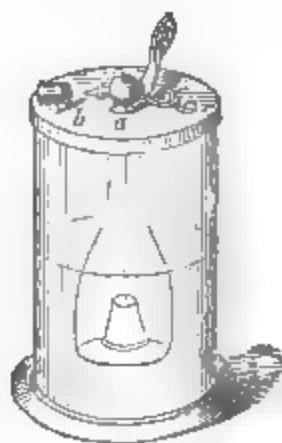


Fig. 44.

478. It has already been mentioned that the flame of hydrogen is very feebly luminous. The highest illuminating power, however, may be conferred upon it by introducing into its flame any infusible solid, which it may raise in temperature. The solid made use of for this purpose is generally quicklime, and the hydrogen is maintained in full combustion by mixing it with oxygen before kindling it. This is most easily and safely effected by conducting hydrogen through one tube, and oxygen

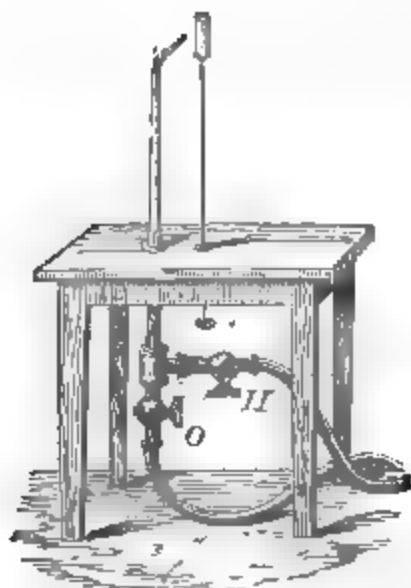


Fig. 45.

through another, from separate gas-holders containing them. These tubes terminate in a single canal, where they are allowed to mix, and from which they are conducted by a jet which directs the cone of flame upon a cylinder of well-burned quicklime (fig. 45). In using this arrangement, the hydrogen is first kindled, and allowed to heat the lime, which communicates to its flame a brick-red colour, owing to the combustion of the metal calcium, of which lime is the oxide. The oxygen is then turned on, when the flame becomes much smaller, and,

from its intense heat, causes the lime to glow with a most brilliant white light. This lime-light, as it is called, rivals sunlight in purity and brilliancy. It is visible on a clear night at a distance of nearly a hundred miles.



Fig. 46.

479. The intense heat evolved during the combustion of hydrogen in oxygen is turned to account in a modification of the arrangement just described, which is distinguished as the oxyhydrogen blow-pipe. In it the tubes conveying the hydrogen and oxygen terminate in a canal, shaped exactly like the letter Y (fig. 46). The oxygen tube joins the one limb, the hydrogen tube the other, and the gases mix in the stalk of the Y, which terminates in a fine aperture like

an ordinary gas jet. The most infusible substances, such as pipeclay and rock-crystal, are melted, or even dissipated, in vapour, if exposed to the flame of the mixed gases. Steel, iron, antimony, copper, bismuth, and all the ordinary metals, burn with great brilliancy, and are, most of them, dissipated as oxides before this blow-pipe flame. The heat it produces far exceeds in intensity or temperature that producible by our most powerful furnaces. It is employed in the arts to melt the refractory metal platinum.

480. Hydrogen and oxygen form two compounds—namely, hydric oxide, or water (formula, H_2O), and hydric peroxide (formula, H_2O_2). The latter is a comparatively rare substance, resembling ozone in the facility with which it gives up its oxygen. Its preparation will be referred to under BARIUM.

481. Water occurs tolerably pure in rain or snow collected in the open country, at a distance from dwellings. It is, as is well known, a colourless liquid without taste or smell. Its ready conversion into ice by the withdrawal of, and into steam by the addition of, heat, has been referred to already in Chapter V. It is a good example of a neutral oxide, having no action on vegetable colours, and being a very stable compound. It dissolves a very large number of substances without altering their properties, and may generally be driven off by heat, leaving the dissolved substance unchanged. For these reasons, it is of exceeding value to the chemist as a solvent. An instance of its use has been given already (page 106), in speaking of the separation of the ingredients of gunpowder, and it is continually employed to separate a crystallisable salt from impurities more soluble than itself. For this purpose, the salt is dissolved in just sufficient hot water (in which most substances are more soluble than in cold water), and the solution left to cool, when crystals of the salt are deposited. This process of re-crystallisation is repeated several times, if a specially pure salt is required.

482. Owing to this solvent power, spring, river, well, lake, mineral, and sea water all contain various substances dissolved

in them which render them unsuitable for many purposes. The composition of a specimen of sea-water and of spring-water is given below.

| 1 kilogramme of sea-water contains : | 1 kilogramme of spring-water contains : |
|--|---|
| Water962.5 | Water.....998.5 |
| Sodic chloride29.0 | Calcic carbonate..... 0.8 |
| Magnesian chloride..... 4.0 | Calcic sulphate..... 0.4 |
| Calcic sulphate 1.5 | Other salts..... 0.3 |
| Other salts (bromides, iodides, } &c.) in small proportion..... } 3.0 | |
| <hr/> 1000.0 | <hr/> 1000.0 |

483. When a water contains calcic carbonate and sulphate, it is called a 'hard' water. The water from chalk districts is invariably of this character, since calcic carbonate (chalk) is dissolved by water containing carbonic dioxide, as all waters do. Soap, when added to such water, is decomposed and loses its cleansing properties, becoming curdled, and refusing to form a lather. A hard water may be partially or wholly purified by boiling, when calcic carbonate is deposited as a 'fur,' or incrustation in the kettle or boiler. The addition of sodic carbonate, or 'washing soda,' as it is termed, will remove the other calcic salts, and thus render the water fit for use. These points will be alluded to again under the heads of CARBONIC DIOXIDE and CALCIUM.

484. The presence of organic matter is a much more serious evil if the water is to be used for drinking purposes ; and many attacks of fever and cholera have been traced to the use of water contaminated with a mere trace of vegetable or animal matter from a sewer or grave-yard. These impurities may be, in general, removed, or rendered harmless, by boiling the water, and filtering it through a charcoal filter ; but it is well to take the opinion of an analytical chemist when a supply is taken from any fresh source for household uses.

485. Water is obtained free from all these impurities by the process of distillation. This has been described already (page 72); and it is only necessary to add that the first portions of water

which come over are likely to contain carbonic dioxide and ammonia, and should be thrown away, if a perfectly pure water is wanted. A water which gives no precipitate or cloudiness when separate portions are mixed with a few drops of solution of (a) baric chloride, (b) argentic nitrate, (c) ammonia and then ammonic oxalate, even after standing for ten minutes, is sufficiently pure for most purposes.

486. *Water of Crystallisation*.—The crystals of many salts contain, even when apparently perfectly dry, a certain amount of water chemically combined,* which seems essential to their crystalline form. To prove this, a crystal of alum may be heated in a tube, when it will melt, and drops of water will condense in the cooler parts of the tube. Some salts, such as borax and sodic carbonate, give up this water even at ordinary temperatures in moderately dry air; while others, on the contrary, as potassic carbonate and calcic chloride, attract moisture from the air, and pass into a liquid. The former are called *efflorescent*, the latter *deliquescent* salts.

Section II.—Nitrogen, The Atmosphere, &c.

NITROGEN.

| | Symbol. | Weight. | |
|---------------|----------------|---------|--|
| Atom..... | N | 14 | 1 litre weighs 1.256 gm. Density = 0.971. |
| Molecule..... | N ₂ | 28 | |

487. *Distribution*.—Nitrogen constitutes four-fifths, or 79 per cent., of air by volume. It is present in the native nitrates or nitres, saltpetre (potassic nitrate), and cubical nitre (sodic nitrate). It occurs also in coal, and in a few other minerals, and is a constant ingredient of plants and animals.

488. *Name*.—The term nitrogen signifies the nitre-producer, and was given to this substance in relation to its occurrence in the important substance saltpetre. Azote is derived from α, signifying, in combination, ‘without,’ or ‘deprived of,’ and ζων

* That this is so is proved by the fact that this water is always present in the proportion required by the law of multiple proportion (page 111). We always obtain from 1 molecule of the salt, 1, 2, 3, &c. molecules of water, and not any fractional proportion. Thus, crystallised alum consists of 1 molecule of the salt associated with 12 molecules of water, its formula being $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

(zoë), life, and was applied to this substance by the French chemists in consequence of animals dying when introduced into the gas. It is not, however, poisonous, as the name might imply, but destroys life, as water does when an animal is drowned in it, by excluding air, and so occasioning suffocation.

489. *Preparation.*—Nitrogen is prepared in two ways. The one, which consists in heating nitric acid on raw butcher-meat in a retort, does not readily yield it pure. The other, and more convenient method, consists in depriving atmospheric air of the oxygen which forms a fifth part of its volume, and thereby leaving its nitrogen free.

490. For this purpose some combustible, such as hydrogen, sulphur, alcohol, or phosphorus, is allowed to burn in a confined portion of air till it goes out. The combustible should be one whose oxide is soluble in water; thus hydrogen forms water; alcohol, water and carbonic dioxide; sulphur, sulphurous anhydride; and phosphorus, phosphoric pentoxide—all of which dissolve in water. The most convenient combustibles are alcohol and phosphorus. One or other of these is to be placed within a metallic cup, mounted on a pedestal, placed on the shelf or stool of the pneumatic trough, or in a basin of water; or the substance may be placed in a small porcelain dish floating upon the water. The combustible is

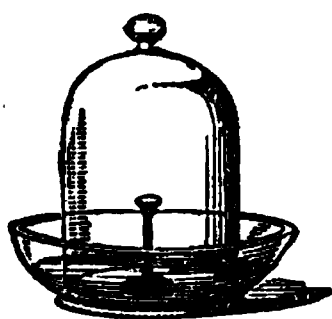


Fig. 47.

then to be kindled, and a jar full of air placed over it. If alcohol be employed, the carbon and hydrogen which it contains rapidly unite with the oxygen of the confined air, and form carbonic acid and water, which are immediately dissolved by the liquid in which the jar stands. If the experiment be made properly, as soon as the alcohol ceases to burn, the water begins to rise within the jar, and ascends till it occupies about one-fifth part of its capacity, replacing the oxygen, which has combined with the alcohol to form water and carbonic dioxide. The gas which remains is the nitrogen of the air. Alcohol has this advantage over most combustibles,

that it leaves the nitrogen colourless, but it frequently ceases to burn before the whole of the oxygen is withdrawn from the air. Phosphorus, accordingly, which removes every trace of oxygen, is generally preferred; but when it is made use of, the nitrogen must be allowed to stand over water till the phosphoric pentoxide, which spreads through it in white fumes, has been absorbed by the water.

491. Nitrogen may also be obtained by passing a slow stream of air over copper turnings heated to redness in a tube, the copper withdrawing the oxygen to form cupric oxide. The apparatus will be described more fully in speaking of the analysis of air (par. 504). An excellent method of obtaining pure nitrogen is to heat a mixture of 16 grms. of potassic nitrite with 10 grms. of ammonic chloride, dissolved in about 50 c.c. of water.

492. *Properties.*—Nitrogen is characterised by the absence of positive properties. It has no taste, colour, or odour; no action upon colouring matter; it neither burns nor supports combustion; and it cannot maintain animal respiration. It is, like oxygen and hydrogen, an incondensable gas, and only slightly soluble in water, 1 litre of which dissolves 15 c.c. of the gas.

493. The only experiment which can readily be tried with it is its action on flame. In relation to combustion, gases are divisible into three classes: (1.) Those which support combustion, of which oxygen is the best example; (2.) Those which are combustible, of which hydrogen is one; and (3.) Those which neither burn nor support combustion, among which nitrogen ranks. A candle introduced into the gas (fig. 48) is at once extinguished without kindling the nitrogen.

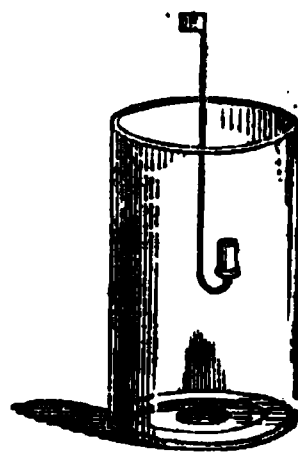


Fig. 48.

494. In reality, however, nitrogen is combustible. This may be proved by mingling it with hydrogen, and kindling the mixture as it issues from a jet into the air. The nitrogen burns to a small extent along with the hydrogen, so that whilst the latter

combines with oxygen to form water, the former unites with both hydrogen and oxygen to form hydric nitrate (nitric acid). Electric sparks or lightning discharges, when they pass through air, determine in like manner the combustion of the nitrogen, and the production of hydric nitrate.

495. Negative as seem all the properties of nitrogen when uncombined, no substance forms compounds possessed of more marked properties, as hydric nitrate and ammonia may serve in the meanwhile to illustrate. Before discussing, however, any of the compounds of nitrogen, it is desirable to consider the constitution of atmospheric air, of which it forms so large a portion.

THE ATMOSPHERE.

496. The air is not a chemical compound, but a mechanical mixture of several gases. The most abundant of these is nitrogen. The next in quantity is oxygen, on which the positive chemical characters of the air, such as its power to support combustion and animal respiration, chiefly depend. Besides these gases, carbonic dioxide, aqueous vapour, ammonia, and ozone are present in small quantities, as well as traces of light carburetted hydrogen, and in towns, sulphuretted hydrogen, and sulphuric dioxide. Minute quantities also of the different volatile compounds which are evolved at the earth's surface, find their way into the atmosphere, but do not permanently affect its constitution.

497. The principal gases are constantly present, and are essential to the maintenance of animal and vegetable life on the surface of the globe. The average composition of air is given below :

| 100 litres of air contain : | |
|-----------------------------|--------------|
| Oxygen | 20.6 litres. |
| Nitrogen..... | 77.9 " |
| Carbonic Dioxide..... | 0.04 " |
| Aqueous Vapour (about)..... | 1.46 " |
| Ammonia | traces. |
| <hr/> | |
| | 100.00 " |

Since, however, the last three ingredients are present in very small and variable proportion, their separation is usually the first process in an analysis of air, and the results are stated without reference to them. Thus, 100 litres of purified dry air contain 79.2 litres of nitrogen and 20.8 litres of oxygen.* In 100 parts by weight of purified dry air there are 77 by weight of nitrogen and 23 of oxygen. The one of these latter numbers is not a multiple of 14, the atomic weight of nitrogen, nor the other of 16, the atomic weight of oxygen, as they should be, if air were a chemical compound.

498. Of carbonic dioxide there are present from 4 to 6 measures in 10,000 of air; and the proportion of ozone is various, being greater in country districts than in towns. The presence of carbonic dioxide in the atmosphere is demonstrated by leaving a shallow vessel containing lime-water in the open air. The lime-water rapidly becomes turbid, owing to the combination of the carbonic dioxide with the lime to form the insoluble calcic carbonate.

499. The amount of aqueous vapour is dependent chiefly upon temperature, so that it varies with latitude, the season, region of the atmosphere, &c.

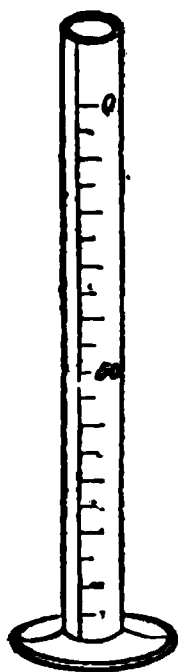
500. The quantity of ammonia (which exists in the air as ammoniac carbonate and nitrate) is small, about one part in one million parts of air; and its presence can only be shewn by operating upon very large quantities of air.

501. The presence of oxygen in the atmosphere is proved by combustible bodies becoming converted into oxides when made to burn in it. Thus hydrogen becomes water, the oxide of that gas.

502. The presence of nitrogen is demonstrated by the result of combustion in confined portions of air, as we have

* Air varies slightly in composition, so that the proportion of oxygen found in it is sometimes a little less than 21, and the nitrogen a little more than 79, volumes per cent. Thus it may contain 20.9 oxygen, and 79.1 nitrogen. It may, however, without serious error be regarded as always presenting the composition stated in the text; and it will be found convenient to call the proportion of oxygen one-fifth, and that of nitrogen four-fifths, of the volume of air.

mentioned whilst describing the method of obtaining free nitrogen.



503. The proportion by volume of oxygen and nitrogen in air may be most simply ascertained by introducing into a tube, graduated into a hundred equal parts, the same number of measures of air. A piece of phosphorus attached to a wire is then to be passed up into the confined portion of air, the tube all the while being kept vertically in the pneumatic trough with its mouth downwards, and under water. The arrangement is to be left undisturbed for twelve hours, during which period the phosphorus, though not kindled, slowly combines with the oxygen of the air, forming an acid which the water dissolves. At the end of the time specified, the phosphorus may be withdrawn, and the volume of gas which remains observed. The water should rise through 21 spaces, replacing the oxygen withdrawn, and leave 79 volumes of nitrogen.*

504. The analysis of air by weight requires a more complicated apparatus. The process by which MM. Dumas and Boussingault (*Ann. Chimie et de Physique*, iii. 257) made their admirable analyses of air, depends on the fact that copper, when heated to redness, readily absorbs oxygen, passing into the state of cupric oxide. The general nature of the apparatus they used will be seen on reference to fig. 50. A is a furnace in which a tube of difficultly fusible glass, BB, filled with pieces of thin copper foil, is heated to redness. At one end of the tube is attached a glass globe, C, and at the other, a series of U-tubes, of which only two are shewn; E containing fragments of pumice, moistened with strong hydric sulphate (sulphuric acid); and F containing fragments of potassic hydrate (caustic potash). The glass globe is exhausted of air, and then weighed. The tube containing the copper, and the

* The results obtained in the above experiment are only approximately exact, since oxygen and nitrogen are slightly, and unequally, soluble in water. For an accurate analysis, the air would be previously purified, as described in the next paragraph, and collected over mercury.

U-tubes, are also carefully weighed. The apparatus is then arranged as shewn, and when the tube containing the copper is red-hot, the stop-cock, G, is partially opened, and a slow stream

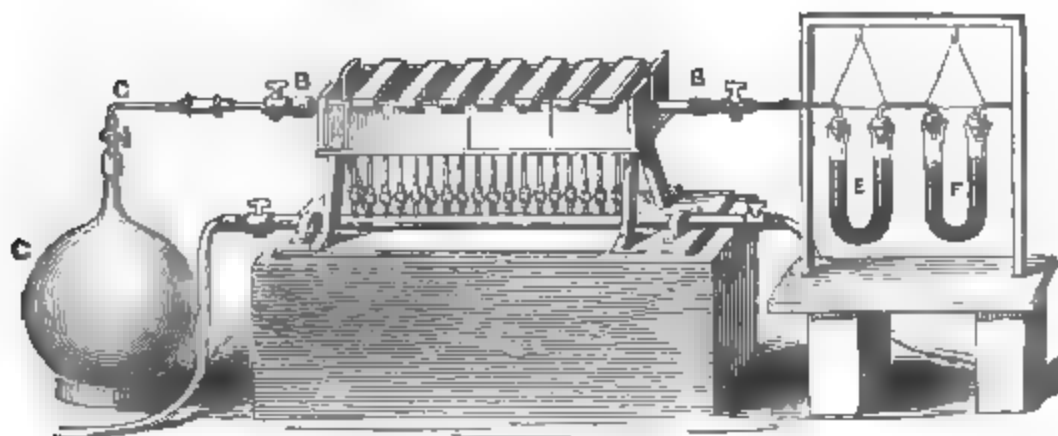


Fig. 50.

of air is thus drawn through the tubes into the globe. The air parts with its carbonic dioxide in the tube F, with its moisture in the tube E, with its oxygen in the tube BB, and nothing but pure nitrogen passes into the exhausted globe, C. When the latter is full, the increase in weight of each part of the apparatus is ascertained. The sum of these increments gives the total amount of air experimented upon, while the several increments give the amount of the different constituents of this air. To take an example: in one experiment the increase in weight of the tube containing the copper was 2.6 grms., of the exhausted globe, 8.73 grms. Neglecting the carbonic dioxide and moisture, the total weight of pure dry air operated upon was therefore 11.33 grms. Then, to express these results in the form of a percentage, we have the proportion:

$$\begin{array}{l} 11.33 : 2.6 :: 100 : 22.94 \text{ per cent. of oxygen.} \\ 11.33 : 8.73 :: 100 : 77.06 \quad \text{ " } \quad \text{nitrogen.} \end{array}$$

505. Ozone is present in the atmosphere to a minute extent, and may be recognised to be there by exposing slips of paper moistened with iodide of potassium and starch, when the paper passes from white to a more or less deep purplish blue,

according to the amount of ozone and the length of time of the exposure. The quantity of ozone in country districts is greater than that in towns, and, indeed, in crowded thoroughfares it ceases to be recognisable. It has a great power of destroying offensive odours, and is believed to be naturally serviceable in oxidising infectious and other deleterious matters which are evolved where animals are congregated together. It is also a powerful bleacher, and is regarded as the agent in the air which whitens clothes when these are sun-bleached. The source of this ozone is not quite clearly ascertained, but it is probably due to the action of plants in decomposing carbonic dioxide and liberating oxygen, as mentioned below. Dr Daubeny (*Journ. Chem. Soc.* xx. 8) has shewn that, when a growing plant is exposed to the light under a bell-jar, the air in contact with it acquires a perceptible quantity of ozone.

506. The uses of the several gases and vapours mentioned are now pretty well ascertained. The importance of water-vapour to animal and vegetable life does not call for lengthened illustration. The oxygen supports the respiration of animals, entering their bodies by their lungs or other breathing organs, and effecting changes on the fluids and tissues, essential to the maintenance of life. Oxygen also enters plants, dissolved in the water which they absorb by their roots.

507. The nitrogen of the atmosphere serves to dilute the oxygen to the point or strength most suitable for the wants of living beings. Animals made to breathe pure or undiluted oxygen are thrown into a state of fever, which quickly proves fatal. Nitrogen, however, also serves an important purpose in the economy of nature, by increasing the volume of the atmosphere without conferring upon it active chemical properties. Provision is thus made for the occurrence of winds, the tempering of climate, the diffusion of heat, the scattering of the sun's light, and the realisation of other useful ends essential to the welfare of man and the other living inhabitants of the globe.

508. The carbonic dioxide supplies plants with their most

abundant element, which they obtain from it by decomposing it into its constituents, carbon and oxygen; the former they retain, the latter they restore to the atmosphere. This decomposition is effected chiefly by the leaves, but also by the other green parts of plants. It occurs only during the day; and to the greatest extent when the sun is shining most brightly. During darkness, plants totally lose the power of decomposing carbonic dioxide. This remarkable action of living vegetables will be referred to again under the head of CARBONIC DIOXIDE.

509. The ammoniac salts which are constantly reaching the air, as products of the decomposition of animal and vegetable matters, are brought down to the earth, as we have seen, by each shower that falls; and, entering the roots of plants along with the rain-water, supply them with nitrogen, an element essential to their growth.

510. The physical properties of the atmosphere are of as much interest as the chemical, but cannot be discussed at length here. The height of the atmosphere is about seventy-two kilometres (forty-five miles)—that is to say, it spreads from the earth in every direction to that extent, so that our globe may be compared to a cannon-ball enclosed in a sphere of glass. The density of the atmosphere, however, is not the same throughout, but rapidly diminishes as we recede from the earth, its lower strata being compressed by those above them, so as to contain within the same volume a much greater weight of air. Were the atmosphere of uniform density throughout, and its density the same as it is at the surface of the sea, its height above the earth would be only eight instead of seventy-two kilometres, as it actually is.

511. The density of air, as we have already mentioned, when treating of specific gravity, is estimated at 1.000, and it is the standard of comparison for the specific gravities of gases and vapours. It is 810 times lighter than water, and 11,000 times lighter than mercury. Nevertheless, its quantity is so considerable that it exerts a great pressure on objects at the surface of the earth. This pressure, at the level of the sea, is equal in

amount to rather more than a kilogramme (1033 grms.) upon every square centimetre, or fifteen pounds on each square inch, or to the weight of a column of mercury 760 mm. in height, or one of water nearly ten metres. This pressure is constantly varying, however, even at the same level, as the risings and fallings of the barometer enable us to mark and to measure.

512. The air, as we have particularly mentioned, is a mechanical mixture, not a chemical compound. The chief reasons for believing it to be so are the following: (1.) The amount of oxygen and nitrogen in it are not such as the law of multiple proportion (page 111) requires, and are not absolutely invariable. (2.) When nitrogen and oxygen are mixed in the proportions in which they form air, no heat is observed to be produced (page 104), and the mixture has all the properties of air. (3.) Air can be separated into its constituents by such mechanical means as solution (like gunpowder, page 106). Oxygen is more soluble in water than nitrogen, and air which has been standing over water is observed to contain less oxygen than ordinary air. Nevertheless, air is exceedingly uniform in constitution. No difference has been detected in the composition of air in one part of the world as compared with another; nor does air brought from the summits of high mountains, or the greatest elevations accessible to balloons, appreciably differ from that in the lowest valley or the deepest mine. The atmosphere, moreover, of unhealthy districts, such as the Campagna of Rome, appears identical in chemical constitution with that from the most salubrious localities, or from above the sea. These remarks apply chiefly to the nitrogen, oxygen, and carbonic acid of the air; and they lead to the discussion of a very important law, which regulates the mixture of gases with each other.

DIFFUSION OF GASES.

513. If the gases of the atmosphere were combined chemically, its uniformity in composition would not surprise us; neither would this be remarkable if the gases had the same

densities ; but we have already seen that their specific gravities are very different. The following numbers illustrate this :

| Gas. | Specific Gravity. |
|-----------------------|-------------------|
| Air..... | 1.000 |
| Nitrogen..... | 0.972 |
| Oxygen..... | 1.105 |
| Carbonic Dioxide..... | 1.529 |

Where the densities are so different, we should expect that the gases would arrange themselves in the order of their densities ; so that the lightest of the three, the nitrogen, should accumulate in the upper regions of the atmosphere ; and the heaviest of them, the carbonic dioxide, be found preponderating at the surface of the earth ; whilst the intermediate oxygen occupied the middle space between the nitrogen and carbonic dioxide. Liquids which do not act chemically on each other invariably arrange themselves in layers according to their densities : thus oil, water, and mercury, even if shaken together, would speedily dispose themselves in strata, with the oil highest, and the mercury at the bottom. No such separation of the atmospheric gases takes place. A long shut tube full of air, kept for many months in a vertical position, is found to contain the gases mixed in the same proportion throughout its whole length.

514. What is still more curious, gases differing much more in relative density than those of the atmosphere, will uniformly mix with each other, although the heaviest be placed lowest. In illustration of this, the following instructive experiment may be tried : Fill one bottle at the pneumatic trough with carbonic dioxide, and another with hydrogen, closing their mouths afterwards with corks or stoppers. Place the bottle of carbonic dioxide standing on a table, and fix into its mouth, by means of a perforated cork, a glass tube two or three inches long, having attached to its upper extremity a second cork, fitting the mouth of the hydrogen bottle, into which it is to be inserted, the hydrogen

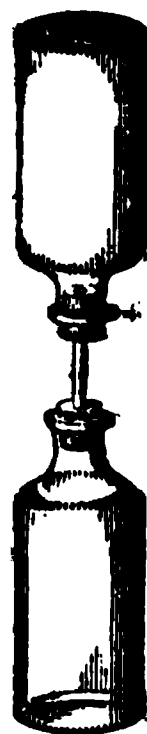


Fig. 51.

bottle having its mouth turned downwards. The bottles thus arranged, as in the foregoing figure (fig. 51), are to be left undisturbed for an hour or more. Carbonic dioxide is twenty-two times heavier than hydrogen, yet it ascends through it, the greatly lighter hydrogen simultaneously descending through the heavier gas, till ultimately an exactly uniform mixture of the gases is contained in the bottles, and this notwithstanding the narrowness of the tube which connected them. The presence of carbonic dioxide in the upper bottle (originally filled only with hydrogen) may be shewn by pouring into it lime-water, which will immediately become milk-white, owing to the production of calcic carbonate. The presence of hydrogen, in like manner, in the lower bottle (at the beginning of the experiment occupied solely by carbonic dioxide), may be demonstrated by transferring its contents at the pneumatic trough to a gas-jar, and adding a little air or oxygen. The hydrogen will then burn on applying a flame. If oxygen be not added, the carbonic dioxide prevents the combustion of the hydrogen.

515. Another experiment, which is, perhaps, better suited for demonstration to a class, is the following: Moisten a piece of blotting-paper, about 20 cm. square, with solution of turmeric, and spread it upon a large plate. Place over it a deflagrating jar (fig. 39), and connect the neck of the latter with a bottle of ammonia gas by a piece of tube, about 1 cm. in internal diameter, and 6 or 8 cm. long. The arrangement will then appear like fig. 51, the deflagrating jar being in the place of the lower bottle. Ammonia is much lighter than air, its density being 0.59, yet in two or three minutes it will have passed downwards through the air in the deflagrating jar, and the yellow turmeric paper will turn brown.

516. These simple experiments shew that gases are under the influence of a force powerful enough to resist the influence of gravitation, and to prevent its taking effect upon mixtures of gases as it does on mixtures of liquids. It has been named *the force of gaseous diffusion*; and the spreading of gases through

each other, against the force of gravity, is spoken of as their mutual *diffusion*.

517. It is this diffusive force which maintains the atmosphere uniform in constitution ; both by retaining in a state of mixture gases which have once mingled, and by causing the uniform diffusion through the atmosphere of every gas and vapour which reaches it, whether it be light or heavy. Thus when hydrogen is allowed to escape from a balloon, it does not ascend to the upper regions of the atmosphere, but diffuses equally through it in all directions. In like manner the carbonic dioxide which the combustion of fuel on the earth is constantly throwing into the air, does not remain at the surface, or descend into pits and mines, but spreads quite uniformly through the whole mass of air. So also the oxygen, which, as we have seen, plants are constantly separating from carbonic dioxide during daylight, does not accumulate around them, but is uniformly mingled with the other constituents of the atmosphere. The air is thus maintained of equal purity throughout. A noxious gas like carbonic dioxide, which would prove injurious if confined to one spot, is thus rapidly diluted, and so rendered harmless ; and a useful gas like oxygen is speedily diffused through the whole atmosphere, so that every living creature equally profits by it.

518. When gases exchange places with each other, in virtue of the force of diffusion, they do not, whilst diffusing, replace each other in equal volumes ; but, on the other hand, a larger volume of a light gas passes in one direction, than of a heavy gas in the opposite. This admits of being illustrated by a simple and very beautiful experiment. A glass tube or cylinder, open at both ends, from one to two feet in length, and from half an inch to two inches in diameter, is closed at one extremity by a plug or plate of stucco,* about 1 cm. in

* Plaster of Paris will answer. The plug may be made by mixing freshly-burned plaster of Paris with water to the consistency of a thick cream, pouring into a basin a sufficient quantity to form a stratum 1 cm. in depth, and then plunging into it the end of the tube, and supporting the latter upright until the plaster has set. It may then be detached from the surrounding plaster, scraped smooth, and dried before a fire.

thickness, and well dried. Stucco, when dry, is traversed by a multitude of very fine pores or canals, through which gases pass readily. At the same time it affords a certain amount of obstruction to their passage, which enables the law regulating their diffusion through each other, when of different densities, to be observed.

519. Such a cylinder as we have described is to be filled with hydrogen, but not at the water pneumatic trough, as this would wet the stucco, which then becomes impervious to gases. The cylinder is most conveniently filled by holding it over a vertical tube proceeding from a gas-holder—a large jar, or bag full of hydrogen. The tube from which the hydrogen is issuing

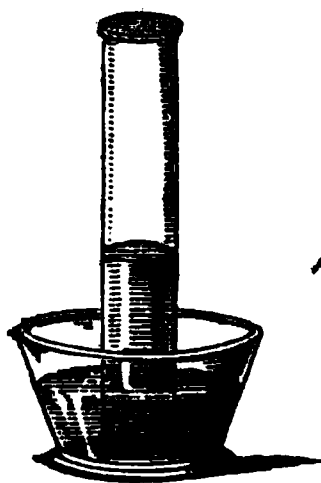


Fig. 52.

is passed up till it almost touches the stucco plate, over which a square of window or plate glass is laid whilst the gas, which is supplied in a rapid stream, is displacing the air. When the cylinder is full of hydrogen, the tube is quickly withdrawn, and the mouth of the cylinder closed by a gas-tray. This is retained in its place by one hand, whilst a finger of the other is laid on the glass plate covering the stucco, till the cylinder has been transferred, with its open end downwards, to a basin of coloured water. The tray and glass plate are now removed, and the eye fixed on the surface of the liquid within the cylinder. The plate of stucco is now in the condition of a porous screen or partition, on the upper side of which there is one (complex) gas—namely, air—and on its lower side another—namely, hydrogen—which is more than fourteen times lighter. The gases immediately begin to exchange places through the stucco; but, in virtue of the law we have mentioned, a much larger volume of the lighter hydrogen ascends in the one direction, than of the heavier air descends in the other. Thus, whilst nearly four cubic centimetres (3.83) of hydrogen leave the tube, only one cubic centimetre of air enters it. The water, accordingly, rapidly rises to fill the space previously occupied by the hydrogen, which has not been

replaced by an equal volume of air. For every four cubic centimetres (or nearly so) which escape, the water rises three cubic centimetres, being forced upwards by the pressure of the air acting on the liquid in the basin.

520. If the cylinder, when filled with hydrogen, were covered by a large bell-jar full of oxygen, then exactly four cubic centimetres of hydrogen would leave the tube for each cubic centimetre of oxygen that entered it. These numbers—namely, 4 in the case of hydrogen, and 1 in that of oxygen—are inversely as the square roots of the densities of these gases, for oxygen is exactly sixteen times heavier than hydrogen, or their relative densities are as 16 (O) to 1 (H), whilst the square root of 16 is 4, and that of 1 is 1. If the gases replaced each other in volumes, which were *as* the square roots of their densities, we should have four cubic centimetres of oxygen entering the stuccoed cylinder for one of hydrogen that left it; and the water, if originally standing at some height within the cylinder, would descend instead of ascending. Exactly the reverse of this we have seen to be the case. It is the hydrogen which gives four cubic centimetres, whilst the oxygen returns only one. Or the replacing volumes are not *as*, but *inversely as*, the square roots of their densities.

521. It is the same with other gases, so that it can be announced, as a general law, that the *diffusion-volumes* of gases—that is, the volumes in which they replace each other in a given time—are inversely as the square roots of the densities of the gases. If this particular law be forgotten, the more general one may be remembered, that, when light and heavy gases are exchanging places, a larger volume of the light gas passes in the one direction than of the heavy gas in the other.

522. The spread of infectious diseases, the ventilation of apartments, the maintenance of animal respiration, and other important natural and artificial processes, are controlled by the law of gaseous diffusion, which belongs more strictly to physics than to chemistry, but cannot be omitted from any treatise on the latter.

Section III.—Compounds of Nitrogen with Hydrogen and Oxygen.

AMMONIA.

| | Formula. | Weight. | |
|---------------|----------------------|---------|---|
| Molecule..... | H_3N | 17 | 1 litre weighs 0.763 gm. Density = 0.59. |

COMPOSITION.

1 litre yields :

$1\frac{1}{2}$ litre of hydrogen, weighing 0.135 gm.
 $\frac{1}{2}$ a litre of nitrogen, " 0.628 "

523. *Distribution.*—Ammonia, as already observed, exists in the air, chiefly as ammonic carbonate. It is a constant ingredient in rich soils, especially clayey soils, which have a remarkable power of absorbing it. As ammonic chloride (sal-ammoniac), it occurs native in volcanic districts. Finally, it is found in manures and other animal excretions.

524. *Name.*—It has received its name from the substance which yields it most readily—namely, ammonic chloride. This was called by the Romans *sal ammoniacum*, or the Ammonian salt, because it was obtained from a district in Libya, where Jupiter Ammon, or rather a corresponding Egyptian deity, Amun, was worshipped. It was called by the alchemists spirits of hartshorn, because they obtained it by the distillation, in close vessels, of deer's horns. Ammonia is also called the volatile alkali. All these names are still in use.

525. When coals are decomposed by heat, as in the manufacture of coal-gas, much ammonia is produced from the combination of the nitrogen and hydrogen of the coal. When bones are similarly treated in the manufacture of bone-charcoal, the same substance results; in both cases, however, in a state of great impurity. The gas or bone-liquor is mixed with hydric chloride (hydrochloric acid), which decomposes the ammonic carbonate and sulphide, forming ammonic chloride (sal-ammoniac). This salt is purified by repeated solution, crystallisation, and sublimation, and is then ready to yield ammonia.

526. About 30 grms. of sal-ammoniac are reduced to powder, mixed with an equal weight of quick-lime, and heated in a retort, or flask with a bent tube. Ammonia, in the state of gas, is evolved abundantly; and being very soluble in water, must be collected at the mercurial pneumatic trough, or by displacement of air. As it is only about half as heavy as the latter, jars or bottles to be filled with it must be held above the tube from which it is issuing, and may be supported in a retort-stand, as shewn in fig. 53. The gas then rises to the highest part of the bottle, and gradually fills it, driving down the air before it, and finally overflows at the neck. The bottle should not be considered full until a piece of yellow turmeric paper, held just above the neck, is at once turned brown by the overflowing gas. It is advisable to close the mouth of the bottle partially by a card, to prevent the entrance of currents of air.

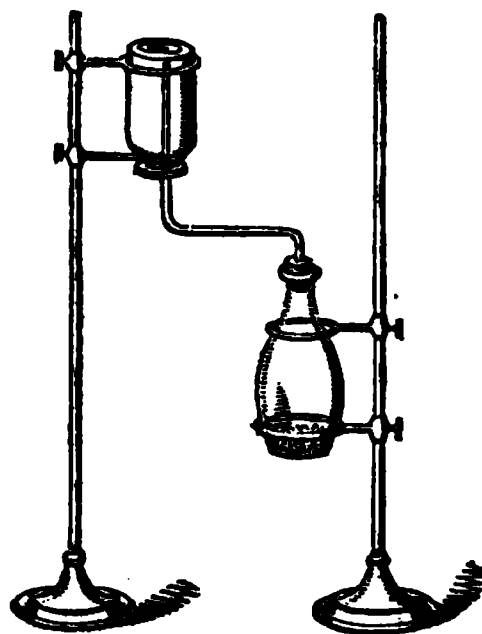
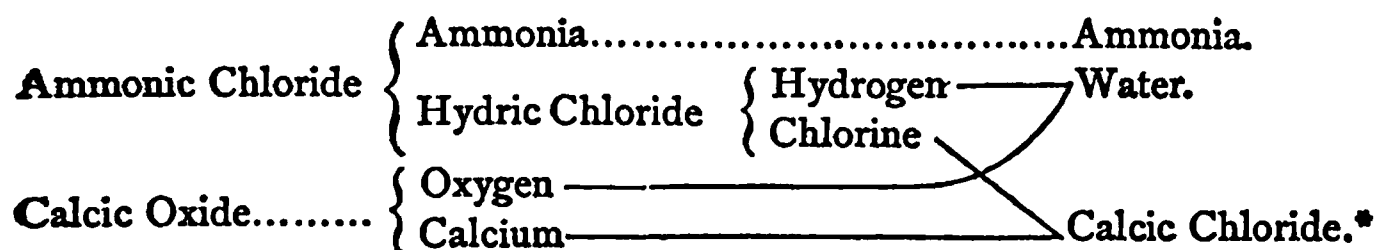


Fig. 53.

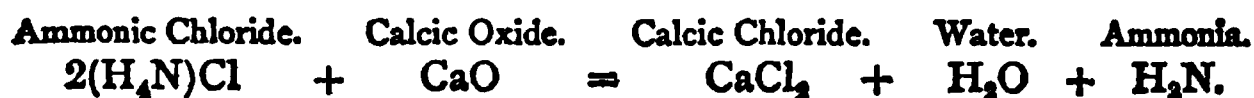
527. The following diagram will explain the decomposition which goes on in the flask :



528. The following experiments may be tried with this important and curious gas, in illustration of its chief properties :

(1.) Its odour is familiar to all as that of smelling-salts, or spirits of hartshorn. It is best observed by contrasting the absence of odour which characterises sal-ammoniac, with the

* The change may be thus expressed in the form of an equation :



immediate development of the hartshorn-smell which attends the addition to it of moist quicklime or potass.

(2.) Its harsh alkaline taste must be tried with a dilute solution of the gas.

(3.) When a lighted taper is passed up into a jar of ammonia, it goes out, but the gas shews a tendency to burn with a greenish flame. Its combustibility is much more marked when it is in contact with oxygen instead of air. A jet of ammonia may be burned in a jar of oxygen, or if a stream of oxygen is caused to bubble quickly through a strong solution of ammonia warmed in a flask, the mixed gases may be kindled at the mouth of the flask.

(4.) Its alkaline action on colouring matter appears when pieces of paper stained with turmeric, rhubarb, reddened litmus, or the purple cabbage, are exposed to the gas. The first two become brown, the third blue, and the fourth green. The same effects are produced by sending a current of the gas through infusions of these colouring matters.

(5.) Water at 15° can dissolve about 700 times its volume of ammonia. To illustrate this, a bottle is filled by displacement with the gas, which is evolved most quickly by boiling in a flask with a long bent tube (see fig. 53) a small quantity of the strong aqueous solution of ammonia, sold by apothecaries under the title of *aqua ammoniæ fortissima* (strongest ammonia-water). The bottle, after being filled, is closed with the thumb, and opened under the surface of water coloured with the infusion of cabbage. The water rushes up with great violence, changing its tint as it ascends from purple to green.

(6.) When ammonia encounters any of the volatile acids, white fumes are produced. These may be readily observed by rinsing a bottle with hydric chloride, and inverting it over a bottle containing a little of the strongest ammonia-water. The fumes are occasioned by the combination of the acid and volatile alkali to form sal-ammoniac.

(7.) Ammonia forms a splendid azure-blue compound with salts of copper. To produce it, a small quantity of solution of

cupric sulphate is added to a glass of water, and a stream of gaseous ammonia sent through it, or ammonia-water is added drop by drop. In either case, the first effect of the addition of the ammonia is to produce a greenish-blue precipitate; but when more ammonia is supplied, this is re-dissolved, and an azure solution produced.

529. By any of those characters, ammonia, when uncombined, may be recognised, but the most readily observed and the most delicate are its odour, and its action as a gas on colouring matter, both of which are eminently distinctive.

530. Ammonia may be liquefied either by cold or pressure. At ordinary temperatures, it requires a pressure of about 7 atmospheres to render it liquid, and the same result is obtained by cooling it to -40° C. By a further reduction of temperature (to -75° C.) it may be frozen into a transparent solid.

531. When a stream of electric sparks is passed through a jar of dry ammonia standing over mercury, the volume of the gas is gradually doubled, and the tube is found, on examination, to contain a mixture of 3 volumes of hydrogen and 1 volume of nitrogen. In other words, 1 litre of ammonia yields $1\frac{1}{2}$ litre of hydrogen and half a litre of nitrogen. From the known densities of these gases, it is easily calculated that 17 parts by weight of ammonia contain 14 parts of nitrogen and 3 parts of hydrogen. Moreover, it is found possible to take out successively one-third, two-thirds, and the whole of the hydrogen from ammonia, and replace it by other radicles, while no such division of the nitrogen has been effected. The best examples of this replacement are to be found in some organic compounds, and cannot well be described here: but the results lead to the belief that the molecule of ammonia consists of 3 atoms of hydrogen associated with 1 atom of nitrogen, its formula being HHHN , or H_3N .

532. Ammonia, in association with a molecule of water, rivals, in many of their properties, potass and soda. Like them, it unites with acids, and forms salts; but, when free from water, it does so without eliminating the hydrogen from the acid. The

constitution of these salts will be considered in connection with those of potassium and sodium.

NITRIC ANHYDRIDE, OR PENTOXIDE.

| | Formula. | Weight. |
|---------------|------------------------|---------|
| Molecule..... | N_2O_5 | 108 |

533. This oxide is scarcely known in a free state, its preparation being difficult, and the substance itself very unstable and explosive. It is formed in small quantity, as mentioned below, by passing a stream of electric sparks through air. It was prepared by Dumas by leading a slow current of dry chlorine gas over powdered argentic nitrate (nitrate of silver), heated gently in a tube. It is then obtained in the form of transparent colourless crystals, which melt at 30° and boil at 45° , undergoing decomposition at a slightly higher temperature. It combines rapidly with water, forming a corrosive liquid, the hydric nitrate described in the next paragraph.*

HYDRIC NITRATE, OR NITRIC ACID.

| | Formula. | Weight. | Density of liquid, 1.52 . |
|---------------|----------------|---------|-----------------------------|
| Molecule..... | HNO_3 | 63 | Boiling-point, 86° . |

534. This acid has been known from an early period, and still retains, as one of its titles, the appellation of aquafortis, given to it by the alchemists. It is found in the atmosphere in small quantity, especially after thunder-storms. It is believed to be produced as a result of the lightning-discharges (as it can be produced on the small scale by sending electric sparks through air), and to unite, after its formation, with the ammonia present in the atmosphere, so that it is found in rain-water as ammonic nitrate. An experiment illustrating its production may be made as follows: Place a little water, tinged blue with litmus solution, in a wide-mouthed litre bottle. Fit to the bottle a cork through which two platinum wires pass, reaching about half-way down the bottle, their ends bent slightly towards each other, but



separated by an interval of about 1 cm. Connect the other ends of the wires with the poles of an induction coil, and pass a stream of sparks through the air in the bottle for three or four minutes. The nitrogen will unite with oxygen to form nitric pentoxide, and this will combine with the moisture present to form hydric nitrate, which will redden the solution of litmus, when the bottle is shaken.

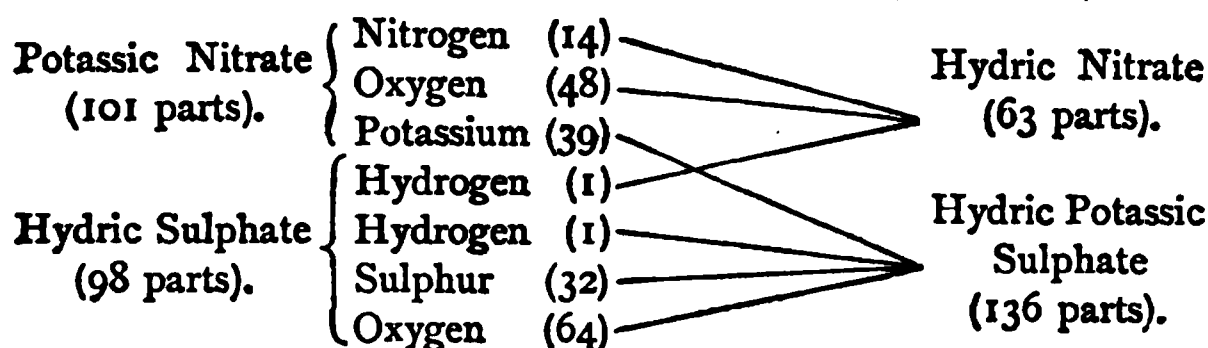
535. The most usual source of hydric nitrate is saltpetre or nitre (potassic nitrate), which occurs in the surface soil in some parts of India, and is also formed artificially by the decomposition of animal matter (see under POTASSIUM).*

536. On the small scale, hydric nitrate is most conveniently prepared by distilling together in a glass retort connected with a receiver (see fig. 18, page 73), equal weights of potassic nitrate and hydric sulphate. About 30 grms. of each are sufficient for the experiment. The action consists in the exchange of potassium for hydrogen. Thus we have :

Before decomposition—potassic nitrate and hydric sulphate.

After decomposition—hydric nitrate and potassic sulphate.

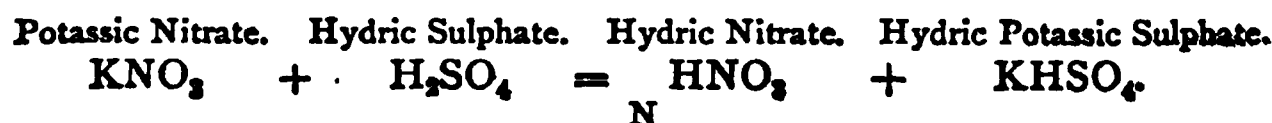
Or, in a diagram : †



The hydric nitrate distils over into the receiver, where it condenses ; the hydric potassic sulphate (bisulphate of potass) remains behind in the retort, and crystallises as the liquid cools. By the employment of one-half the quantity of hydric sulphate,

* The occurrence of nitrates in well-water is due to a similar oxidation of animal and vegetable matter, derived in general from sewage.

† The change may be expressed in symbols :



and at a higher temperature, the hydrogen in the hydric potassic sulphate may similarly be exchanged for potassium, and more hydric nitrate formed, while another salt, neutral potassic sulphate, is obtained.*

537. All nitrates yield hydric nitrate when distilled with hydric sulphate. Sodic nitrate (Chili saltpetre), however, is the only other salt sufficiently abundant and cheap to be used on the large scale. The apparatus used by the manufacturer is a large iron retort lined with fire-clay in the upper part, and

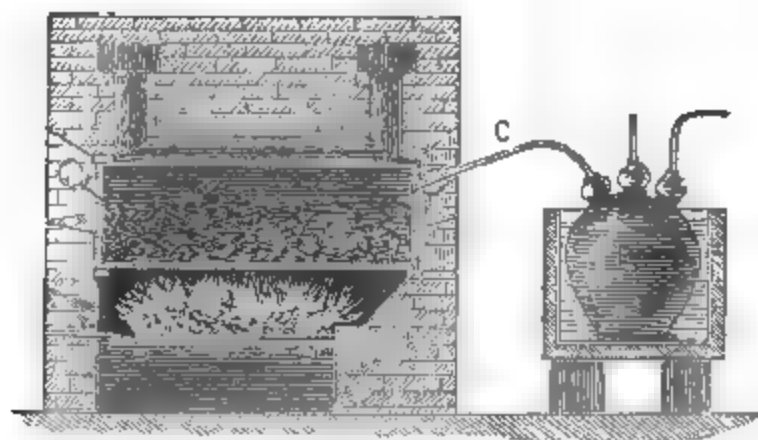


Fig. 54.

set in a furnace (fig. 54). The hydric nitrate, evolved by the action of common hydric sulphate on sodic nitrate, is condensed in a series of stoneware receivers, one of which is shewn in the figure.

538. *Properties.*—Nitric acid is a colourless, transparent liquid when quite pure, but generally exhibits a straw or yellow tint. Its density, when strongest, is about 1.52 (compared with water, 1.000). It has a peculiar odour, a very sour taste, and is exceedingly corrosive. It dissolves nearly all the metals, except gold and platinum; combines with all the basic oxides and other bases, forming, by so doing, an extensive and important series of salts; and acts with the greatest energy on the majority of organic substances, converting them into new and generally remarkable compounds. It is of constant use



in the laboratory, especially as a solvent of metals, and of ores and other minerals.

539. The following experiments will exhibit all its more striking properties :

(1.) Its odour should be noticed, and its taste, after it has been greatly diluted.

(2.) Its effect on colouring matter may be observed by adding a few drops to infusion of litmus, or of the purple cabbage, either of which it will redden.

(3.) It stains the skin and other animal substances yellow, as may be well seen by dipping white wool or worsted into the acid.

(4.) If iron, zinc, or copper, in filings or small fragments, be thrown into it, it evolves a dark-brown or ruddy gas (nitric peroxide). This property is highly characteristic of nitric acid.

(5.) A grain or two of morphia (a crystalline substance prepared from opium), or any of its salts, if added to this acid, give it a dark orange colour, soon fading into yellow.

(6.) A weak solution of indigo in hydric sulphate (the ordinary sulphate of indigo of the shops) has its blue colour destroyed by hydric nitrate, especially if the liquid be heated.

(7.) When solution of ferrous sulphate (green vitriol) is added to hydric nitrate (best after the addition of some strong hydric sulphate), a dark-brown liquid is formed, which becomes light yellow, with evolution of gas, when boiled (see par. 559). This is the most characteristic test for hydric nitrate.

540. The word 'test' constantly occurs in chemical works, and its meaning may be explained here, on our first occasion of using it. A test is a material for some experiment intended to bring out a property characteristic of the substance under examination, and by which the presence of that body may be detected. Thus, no liquid but hydric nitrate gives ruddy fumes when certain metals are added to it: hence these metals, such as copper and zinc, are tests for hydric nitrate.

541. A large series of salts, called NITRATES, are formed by the substitution of other basic radicles (par. 317, page 122) for the

hydrogen in hydric nitrate. Only one salt, however, is formed by each radicle, the hydrogen of the acid being taken out altogether, when it is taken out at all. Hence hydric nitrate is called a 'monobasic' acid.

542. All the lower nitrogen oxides are prepared directly or indirectly from hydric nitrate. We proceed to take them in descending order.

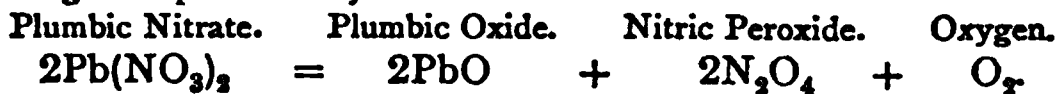
NITRIC PEROXIDE OR TETROXIDE.

| | Formula. | Weight. | I litre weighs at 97°, 2.306 grms. | |
|---------------|----------|---------|------------------------------------|---|
| Molecule..... | N_2O_4 | 92 | " | " |
| | | | 4°, 3.347 | " |

543. When hydric nitrate is caused to act upon the metal lead, the latter is dissolved with evolution of a mixture of nitrogen oxides, and on evaporation of the solution, white crystals of a salt called plumbic (lead) nitrate are obtained. This salt, when thoroughly dried at a temperature a little above 100°, and then further heated in a retort or flask (which should be made of infusible glass), is decomposed into plumbic oxide (litharge), oxygen gas, and nitric peroxide.*

544. This substance is, at summer temperatures, a gas of an orange colour, the intensity of the colour becoming remarkably increased when the temperature is raised. By a slight reduction of temperature—for instance, by passing the gas through a U-tube immersed in a basin of cold water (which should have a few lumps of ice in it)—it is condensed into a yellow, very volatile liquid, boiling at 22°, and freezing into a crystalline solid at - 30°. This liquid is yellow only if quite free from moisture. If a mere trace of water is present, it is green; and if a little water be added, drop by drop, it becomes deep blue, and then colourless, giving off bubbles of gas (nitric dioxide), while hydric nitrate remains in the liquid.†

* The change is expressed in symbols:



† The first action probably consists in the formation of hydric nitrate and nitrite.



Then the hydric nitrate, an unstable substance, is decomposed.



NITROUS ANHYDRIDE OR NITRIC TRIOXIDE.

| | Formula. | Weight. |
|---------------|----------|---------|
| Molecule..... | N_2O_3 | 76 |

545. This oxide is not of any great interest. It is an orange gas produced by gently heating hydric nitrate with arsenious anhydride (common white arsenic), or with starch. It may also be obtained by mixing 4 measures of nitric oxide with 1 measure of oxygen, and may be condensed into a liquid by a cold of -30° . It combines readily with water, forming an acid, hydric nitrite.* This acid is the type of a series of salts, called nitrites, chiefly noticeable for the readiness with which they give up oxygen. From this property, potassic nitrite is often used in the laboratory as an oxidising agent (see, for instance, IODINE). It may be obtained by passing the gas into solution of potassic hydrate, until the liquid is neutral, or only slightly alkaline.

546. An interesting experiment, illustrating the formation of a nitrite by the oxidation of ammonia, may be made as follows. Pour a few drops of strong solution of ammonia into a flask or bottle, and shake it up to diffuse the gas through the air. Twist a piece of platinum wire, about 20 cm. long, into a spiral, leaving about 6 or 7 cm. straight, and attach it to a strip of card which will just fit vertically into the neck of the flask. Heat the spiral to redness, and plunge it into the mixture of ammonia and air in the flask. White vapours will almost immediately be formed, consisting of ammoniac nitrite, and the platinum will continue to glow for several minutes, owing to the heat produced by the chemical combination of the elements of ammonia with the oxygen of the air.† This is only one of many instances of chemical combination effected by platinum (see under PLATINUM).

* $N_2O_3 + H_2O = 2HNO_2$, hydric nitrite.

† (1.) $2H_2N + 3O_2 = 2HNO_2 + H_2O$.

(2.) $2HNO_2 + 2H_2N = 2(H_2N)NO_2$, ammoniac nitrite.

NITRIC OXIDE OR DIOXIDE.

| | | |
|--------------------------------------|---------|--|
| Formula: | Weight. | 1 litre weighs 1.343 grm. Density = 1.04. |
| Molecule..... N_2O_2 | 60* | |

COMPOSITION.

1 litre yields :

 $\frac{1}{2}$ a litre of nitrogen, weighing 0.628 grm. $\frac{1}{2}$ a litre of oxygen, " 0.715 "

547. *Preparation.*—By pouring hydric nitrate, diluted with an equal volume of water, on copper clippings or filings. A retort, or any of the forms of apparatus employed in the case of hydrogen (see fig. 40), will serve for the preparation of this gas, and it may be collected at the pneumatic trough. The action does not require the application of heat.

548. The reaction is not a very simple one. It would seem that the copper displaces the hydrogen in the hydric nitrate, and this hydrogen, instead of being evolved as gas, remains in combination with some of the oxygen of another molecule of the acid, while the nitrogen and the rest of the oxygen of this molecule are evolved in combination as nitric oxide gas. Thus :

- (1.) Copper and hydric nitrate give cupric nitrate and hydrogen.
- (2.) Hydrogen and hydric nitrate give water and nitric oxide.

549. In this reaction, 198 parts by weight (grammes, ounces, &c.) of copper act upon 504 parts of hydric nitrate, to form 562.5 parts of cupric nitrate, 72 parts of water and 60 parts of nitric oxide. These are the results of experiment, of actual weighing and measuring. But it is possible, if we know all the substances produced, and assume a certain weight and composition for their molecules, to obtain a symbolical expression for the reaction on the principles of the laws of chemical combination.

550. The constitution of the molecules (that is, the smallest

* The weight of the molecule of this substance is uncertain. See par. 405, page 153.

particles which can exist in a free state, page 121) of the above substances is given below :

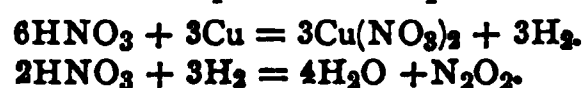
| | | | | | |
|----------------|---|-------------------------------------|--|---------------|---|
| Hydric Nitrate | { | Hydrogen, 1 atom.....H | | Copper.....Cu | |
| | | Nitrogen, 1 atom.....N | | | |
| | | Oxygen, 3 atoms.....O ₃ | | Water | { |
| | | | | | |
| Cupric Nitrate | { | Copper, 1 atom.....Cu | | Nitric | { |
| | | Nitrogen, 2 atoms....N ₂ | | | |
| | | Oxygen, 6 atoms.....O ₆ | | | |
| | | | | Oxide | { |
| | | | | | |
| | | | | | |

Now, since less than a molecule of nitric oxide cannot be produced, and this contains two atoms of nitrogen, therefore 2 molecules of hydric nitrate at least (each containing 1 atom of nitrogen) must be taken. These two molecules, H₂N₂O₆, besides the elements of a molecule of nitric oxide, N₂O₂, contain the elements of a molecule of water, H₂O, and 3 atoms of oxygen, O₃. These three atoms of oxygen require, to form water, 6 atoms of hydrogen, and these must be taken from 6 other molecules of hydric nitrate by the action of the copper, 3 molecules of copper being required for this action. Hence the *minimum* number of molecules which can take part in the action are 3 molecules of copper and 8 (that is, 6 + 2) molecules of hydric nitrate; and these produce, since no weight is lost in chemical combination (page 108), 3 molecules of cupric nitrate, 4 molecules of water, and 1 molecule of nitric oxide. All this may be expressed in the form of an equation (see, for further explanation, page 134) :



551. The above is given as an example of the convenient way in which symbols can be employed to illustrate chemical decompositions. The student should follow every chemical change in a similar way in his note-book, and exercise himself

* This may be considered as made up of the two equations :



It will often be found convenient, in making out chemical equations, thus to assume several stages of the action, and then to combine the results.

in devising instead of copying equations. The problem is: Given the names and composition of the molecules of the substances formed and decomposed, to find the *minimum* number of molecules concerned in the action. The answers to such problems will, obviously, not supersede experimental results, but may sometimes serve to suggest them.*

552. Another excellent method of obtaining pure nitric oxide is, to place in a flask a powdered mixture of 10 grms. of potassic nitrate, and 60 grms. of ferrous sulphate, add 150 c.c. of dilute hydric sulphate (1 part acid to 3 of water), and apply a gentle heat. The mixture is apt to froth up at first, and the action must be carefully watched.†

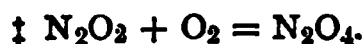
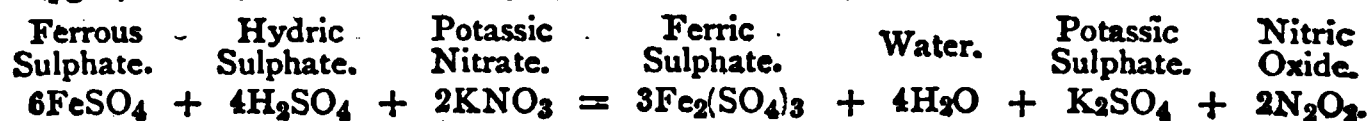
553. *Properties.*—Nitric oxide is colourless and invisible, slightly heavier than air, very sparingly soluble in water, incombustible, irrespirable, and not a supporter of ordinary combustion.

554. It possesses one remarkable and useful property: when it meets air, it gives rise to the production of a dark-brown or ruddy gas—nitric peroxide. This change is owing to its combining with the oxygen of the air;‡ and, as might be expected, the change occurs still more markedly when oxygen instead of air mixes with nitric oxide.

555. The most striking way of exhibiting this property of the gas is to fill a large jar with it at the pneumatic trough, and then suddenly turn its mouth upwards. If, whilst the

* Symbols are much more expressive as used on a black board or slate than as they appear on a printed page, where they all stand at once before the reader, and the *stages* of a decomposition cannot be illustrated. Chalks of different colours may be used in the case of very young pupils, to make the diagrams more manifest; but, on the whole, one colour is preferable, as it can be copied by the pupil with the slate or lead pencil, or pen.

† In this case, ferrous sulphate, a substance which has a great tendency to absorb oxygen, is used, instead of hydrogen, to deoxidise the hydric nitrate.



It must be remarked that the molecule of nitric oxide seems to be twice as large as the molecule of oxygen: so that the above equation, interpreted of volume, will be: Two measures of nitric oxide unite with one measure of oxygen to form two measures of nitric peroxide.

ruddy fumes are in the jar, it be placed with its mouth downwards in a vessel of water, an additional phenomenon is observed: the water dissolves the nitric peroxide, and rapidly ascends within the jar.

556. To observe the effect with oxygen, a jar, half full of nitric oxide is placed upon the stool of the pneumatic trough, and oxygen gas rapidly added to it. This is effected by placing the mouth of the oxygen jar between the limbs or supports of the stool; the mouth of the jar being held downwards till it is completely within the funnel-shaped cavity of the stool. The closed end of the jar is then rapidly depressed, so that the gas it contains is quickly poured up through the funnel, as liquids are familiarly poured down through such an apparatus. (See fig. 55.) The trough-stool is omitted, for simplicity's sake, in the drawing. This experiment is a striking and beautiful one, from the instant development of the dark-coloured gas, and the rapid ascent of the water in the jar.

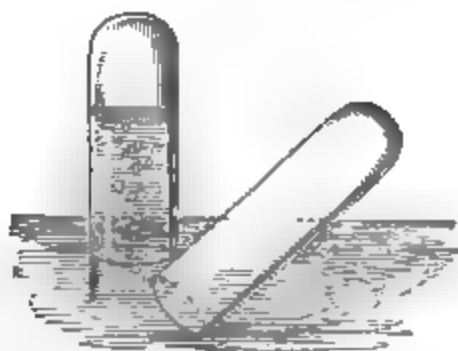


Fig. 55.

557. Nitric oxide thus supplies a very delicate test of the presence of oxygen in any gaseous mixture. It is only necessary to add to the latter, whilst standing over water, a small volume of the gas in question. If oxygen be present, the gas will instantly become coloured. A dark-brown tint will appear if there is much oxygen, a pale yellow if there is only a trace of it. A sheet of white paper held behind the glass vessel enables the eye to detect the slightest production of colour. This reaction is of some interest, since the first series of tolerably accurate analyses of atmospheric air was made by its means, by the English chemist, Cavendish.

558. Although a lighted taper will not continue to burn in nitric oxide, yet it can be shewn to be a supporter of the combustion of some substances. In other words, it will not only combine with oxygen, as shewn in the last paragraph, but

also give up oxygen. Thus, if a piece of phosphorus be heated in a deflagrating cup until it burns *brightly* in air, and then plunged into a jar of nitric oxide, it will continue to burn, and with a brilliancy almost as great as in oxygen. Again, if a few drops of carbonic disulphide be poured into a jar of the gas, and thoroughly shaken up, so as to diffuse the vapour, and a light be then applied, a brilliant flash of bluish light will pass quickly down the jar.

559. Nitric oxide is absorbed by solution of ferrous sulphate with formation of a dark-brown liquid, which gives off the gas on being heated. It is on the formation of this compound that the test for a nitrate (par. 539) depends.

560. When potassium or tin is heated in a known volume of the gas, the metal combines with the oxygen, and half the volume of nitrogen is left. In this way the composition of the gas is ascertained.

NITROUS OXIDE.

| | Symbol. | Weight. | |
|---------------|---------|---------|---|
| Molecule..... | N_2O | 44 | 1 litre weighs 1.971 gm. Density = 1.52. |

COMPOSITION.

1 litre yields :

1 litre of nitrogen, weighing 1.256 gm.
 $\frac{1}{2}$ a litre of oxygen, " 0.715 "

561. *Preparation.*—When solution of hydric nitrate is added by degrees to solution of ammonia, a point is at last reached when the liquid neither turns turmeric paper brown, like ammonia, nor litmus paper red, like hydric nitrate. If, when this is the case, the liquid is evaporated to a small bulk, white crystals of a salt called ammonic nitrate are deposited on cooling. When this salt (about 30 grms. may be taken) is placed in a retort and heat applied, it first melts to a clear fluid, and then, at a slightly higher temperature, is entirely decomposed into nitrous oxide and water. The former may be collected in jars at the pneumatic trough, whilst the water

condenses. The change may be represented by the following equation :



The oxygen of the molecule dividing itself between the hydrogen and the nitrogen.

562. *Properties.*—A colourless invisible gas, possessing a faint, agreeable odour, and pleasant, sweetish taste. It is soluble in about three-fourths of its volume of water: 1 litre of water at 15° dissolving 780 c.c. of the gas; and a solution so prepared has been sold as an exhilarating drink. It is only, however, when it enters the body by the lungs that this gas occasions that peculiar form of excitation which has made it so famous.

563. It supports combustion brilliantly; throws into full flame a red-hot match or paper; and detonates when exploded with an equal measure of hydrogen.* It is distinguished from oxygen by its solubility in water, its odour, and its taste, and principally by its producing no ruddy flames when mixed with nitric oxide, such as oxygen does, and enabling sulphur introduced therein to burn with a beautiful rose tint. The experiments on combustion, which are given under the head of oxygen, can be tried with this gas; but the combustible must in all cases be heated pretty strongly, so as to be in full combustion in air, before being immersed in the gas.

564. The most interesting property of nitrous oxide is its action on the living body. When rapidly respired, it produces a transient, but very pleasant form of excitement, resembling that occasioned by wine or opium. The sensations experienced during the respiration of this gas are generally pleasurable, and are not followed by depression or other unpleasant symptoms. It frequently, however, occasions violent muscular action; and it should never be administered unless in the presence of one or two persons strong enough to resist effectually

* $\text{N}_2\text{O} + \text{H}_2 = \text{H}_2\text{O} + \text{N}_2$.

A volume of nitrogen equal in bulk to the original volume of the gas is left.

the struggles of the person under the influence of the nitrous oxide, otherwise he may injure himself and others.

565. In the great majority of cases no unpleasant result follows the respiration of this gas; but on some persons it acts injuriously, and it cannot be considered safe to administer nitrous oxide in any circumstances, unless in the presence of a medical man. Care, moreover, should be taken that the gas is pure; in particular, that the ammonic nitrate contain no

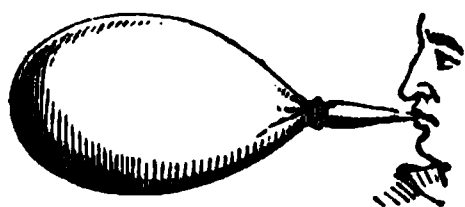


Fig. 56.

chloride; and the salt should not be heated too strongly when collecting the nitrous oxide, otherwise the latter may be rendered irritating by the presence of fumes of ammonic nitrate, and irrespirable products of its hasty decomposition.

566. Nitrous oxide is breathed from a waterproof cloth bag large enough to contain four or five litres, having a wooden tube or nozzle. It is replenished, as wanted, from a gas-holder. The gas is now much used as an anæsthetic agent—that is, to produce insensibility to pain under surgical operations. It is much safer for these purposes than chloroform, although its effects are not so prolonged.

Section IV.—Carbon, and its Compounds with Oxygen, Hydrogen, and Nitrogen.

CARBON.

| Symbol. | Weight. | Density of diamond = 3.3. |
|------------|---------|---------------------------|
| Atom.....C | 12 | " graphite = 2.2. |

567. *Distribution.*—Carbon occurs in nature uncombined, as the diamond, and as the mineral *graphite* or *plumbago*. It is much more abundant, however, in a state of combination. Thus it occurs in union with oxygen in the carbonic dioxide present in the atmosphere, and in combination with oxygen and calcium or magnesium, forms, in the shape of limestone, a large portion of the earth's crust. In union mainly with hydrogen, it is the chief constituent of coal; and, along with oxygen, hydrogen, and nitrogen, it is an abundant ingredient of

animals, and still more of plants. It exists in several 'allotropic' forms; that is, in forms which differ from each other in many physical and some chemical properties, but which, nevertheless, consist of nothing but the single element.*

568. The diamond is the purest form of carbon, and admits of being entirely converted into carbonic dioxide by combustion in oxygen. It occurs in alluvial soils derived from the disintegration of quartz or sandstone rocks, at Golconda, in India, and in Brazil. It is found crystallised in octahedra and other forms belonging to the regular system (page 36). Owing to its hardness, it is much employed for cutting glass, for which purpose a natural edge of the crystal must be used. From its transparency and high refractive power for light, it is much valued as a gem; and is cut into various forms by its own dust, nothing else being hard enough to grind it. It has never been fused; but, when heated intensely in the electric arc, it swells up into a black porous mass like coke.

569. Graphite, or plumbago, is the substance so largely employed in the manufacture of pencils. It goes ordinarily by the name of *black-lead*, but it contains no lead. Iron is frequently present, but the purest specimens consist solely of carbon. It occurs in veins, generally in granite and the primary rocks, in various parts of the world, but only a limited portion of it is soft enough to be used for pencils. The coarser varieties have a certain commercial value, being employed as a coating for iron.

570. Various important artificial varieties of carbon are made use of in the arts. They go generally by the name of charcoal. The four most important kinds are *wood charcoal*, *coke*, *animal charcoal*, and *lampblack*.

571. Wood charcoal is prepared by heating wood in iron retorts as long as it evolves anything volatile. The water originally present in the wood, its hydrogen, oxygen, nitrogen, and a large part of its carbon, are expelled in the form of

* The name is derived from two Greek words ἄλλος, other, and τρόπος, mode, character.

various gases and vapours, and the excess of carbon left behind constitutes the wood charcoal of commerce. Charcoal may be made on the small scale by heating a piece of wood to a low red heat in a glass tube. Wood charcoal is employed in the arts, and as a fuel. It is of much use in blow-pipe experiments, and is largely consumed in the manufacture of gunpowder.

572. When coal is treated in the same way, as it is in the manufacture of coal-gas, the excess of carbon is, in like manner, left behind, forming a hard, shining, light solid, highly valued as an economical and powerful fuel. This substance, which is literally charred coal, and therefore best deserves the title of charcoal, goes, nevertheless, by the name of *coke*, the word charcoal, when not qualified by some prefix, being generally understood to signify the carbon of wood.

573. A variety of coke, sometimes called artificial graphite, is found in the upper parts of the gas-retorts, and is probably formed by the decomposition of gaseous compounds of carbon and hydrogen. It is very hard and compact, with an almost metallic lustre, and is a good conductor of heat and electricity. It is much used in place of the more expensive platinum, as the negative element in a galvanic battery, and is the material of which the poles are made, between which the current of a powerful battery is passed to produce the electric light.

574. Animal charcoal is obtained by heating any animal substance in retorts as long as volatile products are evolved. The variety of it best known as an article of commerce is that which goes by the name of ivory-black or bone-black. It is not pure charcoal, but consists of that substance mixed with the non-volatile calcic salts, chiefly calcic phosphate and carbonate, which confer upon fresh bones their hardness and rigidity. These salts are left as a white earthy skeleton, when a bone is heated in an open fire so as to burn away its carbon. Animal charcoal, but especially bone-black, possesses in a remarkable degree a property not altogether wanting in wood charcoal—that, namely, of removing colour from liquids which owe their tint to the presence of animal or vegetable colouring matters.

This bleaching power of bone-black leads to its great consumption by the sugar-refiner, who deprives brown sugar of its colour by filtering through a stratum of coarsely powdered charcoal. It acts still more powerfully if heated with the liquid to be bleached, and it is largely used in this way by the manufacturing and scientific chemist in the purification of organic substances—such, for example, as morphia or quinine.

575. Animal, like wood charcoal, possesses the power of destroying odour as well as colour. The latter is employed, accordingly, to purify tainted water on shipboard, and occasionally to lessen the odour of game which has been over-kept. The decolorising power of animal charcoal may readily be demonstrated by boiling infusion of litmus or cabbage with powdered ivory-black, and then passing the liquid through a paper filter. (See fig. 25, page 107.) It is rendered perfectly colourless.

576. Charcoal, like many other porous substances, has the property of absorbing large quantities of some gases. A piece of it will absorb no less than 90 times its own volume of ammonia, and 50 times its volume of hydric sulphide. Both these gases are evolved from putrefying substances, and it is to the above property that charcoal owes its value as a disinfectant and a material for respirators and filters. To illustrate this property, a long narrow gas-jar may be filled with dry ammonia over mercury, and a piece of charcoal, previously heated to redness to expel the gas its pores contain, should be passed up into the gas. The mercury will almost immediately begin to rise in the jar, shewing that there is an absorption of the gas.

577. Lampblack is the soot of imperfectly burned combustibles. It is prepared by burning tar, or any other inflammable body containing carbon and hydrogen, with a limited supply of air. In such circumstances the hydrogen of the combustible burns, but very little of the carbon is consumed. The greater part of it, on the other hand, is carried up in the state of a finely divided powder in the current of warm air which rises from the burning body. When this warm current of gases impinges

upon a cold surface, it deposits on it the carbon, which is allowed to accumulate, until it has formed a pretty thick layer, when it is scraped off, and forms the lampblack of commerce. This variety of carbon, which, it will be observed, is merely soot or condensed smoke, is very largely employed in the arts in the preparation of black pigments. China-ink is a kind of lampblack made into cakes with gum-water.

578. Carbon, in all its forms, is an exceedingly unalterable substance at ordinary temperatures, so that stakes of wood are charred at their surfaces before being driven into the earth, as a precaution against their decay. If carbon, however, be raised in temperature, it combines with oxygen, as we have seen in speaking of that gas, and by so doing, forms carbonic dioxide, CO_2 , or carbonic oxide, CO , according to the proportion of oxygen supplied to it. Both of these oxides of carbon are compounds of great interest. We begin with carbonic dioxide.

CARBONIC DIOXIDE.

| | Symbol. | Weight. | |
|---------------|---------------|---------|--|
| Molecule..... | CO_2 | 44 | 1 litre weighs 1.966 grm. Density = 1.53. |

COMPOSITION.

1 litre yields :

1 litre of oxygen, weighing 1.430 grm.
 $\frac{1}{2}$ litre of carbon gas (?), " 0.536 "

579. *Distribution.*—Carbonic dioxide occurs, as we have already seen, in the atmosphere, and can be obtained in large quantity from calcic carbonate, which is the constituent of limestone, marble, shells, corals, &c. It is present in all natural waters ; in some of them largely. It issues from the earth in various parts of the world, and is evolved in large quantity by volcanoes. It is a constant product, moreover, of animal respiration, and is given out by plants during darkness. Fermenting liquids, and most animal and vegetable substances whilst decaying, produce it, and the combustion of fuel at the earth's surface is an unceasing source of carbonic dioxide.

580. *Preparation.*—The gas is prepared in the laboratory in two ways. The one is a synthetic process, and consists in burning charcoal in oxygen; the other is an analytic one—namely, the decomposition of various carbonates such as calcic carbonate.

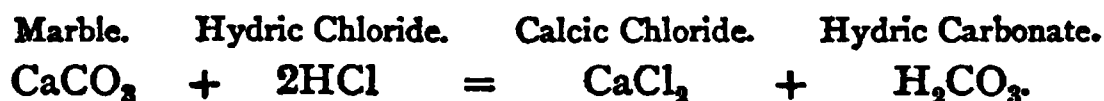
581. We have described, under the head of oxygen, the arrangement required for burning charcoal in that gas. When charcoal is burned in oxygen till the latter is entirely converted into carbonic dioxide, no change in volume occurs, so that a litre, for example, of oxygen, after it is saturated with carbon, forms exactly a litre of carbonic dioxide. Although the oxygen is not increased in volume by its conversion into carbonic dioxide, we need scarcely say that it is altered in weight, so that for every 32 grms. of oxygen, we obtain, in virtue of its combination with 12 grms. of carbon, 44 grms. of carbonic dioxide.

582. The production of carbonic dioxide during the combustion of charcoal is easily demonstrated by adding lime-water to the jar originally full of oxygen in which the charcoal was burned. The lime-water at once becomes milky, from the production of calcic carbonate.

583. The analytic process for carbonic dioxide is the one generally followed. Fragments of broken marble are placed in such a vessel as was used in the preparation of hydrogen or nitric oxide (see fig. 40), and after the addition of enough water to cover the marble, a little hydric chloride (muriatic acid) is poured down the tube-funnel. Carbonic dioxide is evolved with great rapidity, and may be collected over the pneumatic trough, filled with warm water. Any carbonate will yield carbonic dioxide if exposed to the action of the stronger acids, such as sulphuric, muriatic, nitric, or acetic. No carbonate, however, is so convenient as calcic carbonate, in the form of fragments of white marble, and no acid is so suitable as hydric chloride.

584. The evolution of carbonic dioxide by the action of a stronger acid on a carbonate admits of a simple explanation. Marble consists of 1 atom of calcium associated with 1 atom

of carbon and 3 atoms of oxygen, the formula of its molecule being CaCO_3 . Hydric chloride consists of 1 atom of hydrogen and 1 atom of chlorine, its formula being HCl . We may consider that in the first instance there is an exchange of hydrogen for calcium, as represented in the following equation :



But this hydric carbonate is so unstable, that it immediately breaks up into water and carbonic dioxide, thus :



The whole decomposition may then be expressed by combining the two equations thus :



585. *Properties.*—Carbonic dioxide is a colourless, invisible gas, having a peculiar sharp, but not sour, odour and taste. Water dissolves its own volume of this gas—1 litre at 15° dissolving almost exactly 1 litre of the gas—and acquires, in consequence, a sparkling appearance, and refreshing, slightly stimulant taste, such as all are familiar with in soda-water and other effervescing liquors. This solubility of carbonic dioxide in water is nearly the same, whatever be the pressure under which the gas is placed. Thus, supposing a litre of the gas is measured under the ordinary pressure of the air, and afterwards compressed into half a litre, then half a litre of water will dissolve the whole of the gas; but when the extra pressure is removed, half a litre of the gas will escape from the water in multitudes of bubbles. It is to this that the effervescence of soda-water is due—soda-water being simply a strong solution of carbonic dioxide, formed by forcing the gas into water under great pressure. Sparkling wines also contain carbonic dioxide, which is, in such cases, generated by fermentation in the liquid itself.

586. The liquefaction of carbonic dioxide has been already alluded to (par. 205, page 71). It becomes a liquid, at ordinary

temperatures, under a pressure of about 60 atmospheres (60 kilogrammes on a square centimetre). The gas is usually condensed by a powerful pump into a strong wrought-iron bottle, kept cool by a stream of water. When the liquid is allowed to escape from a jet, part of it flashes immediately into gas, and the cold produced by this rapid evaporation (page 70) is sufficient to freeze the remainder of the liquid. It then forms a snow-like flocculent solid, which evaporates comparatively slowly, unless when mixed with ether. By the evaporation of this mixture in a vacuum, a very great degree of cold, about -110° , has been produced.

587. Carbonic dioxide is about half as heavy again as air, its specific gravity being 1.53. It is unflammable, extinguishes combustion, and cannot support animal respiration. It is distinguished from the other irrespirable and incombustible gases by the precipitate, already frequently referred to, which it produces in lime-water. Its properties may be demonstrated by the following experiments: (1.) The odour of carbonic dioxide is best observed by holding the nostrils over soda-water, or a dissolved seidlitz powder, from which the gas is effervescing. (2.) Its taste is best noticed by taking a draught of pure water which has been saturated with it. Such a solution is most easily prepared by half filling a bottle of water at the pneumatic trough with the gas, corking it, and shaking it briskly. The carbonic dioxide is immediately absorbed by the water, as may be proved by quickly withdrawing the cork, when the sound of air rushing in to fill the vacuum left by the absorbed gas will be heard. This experiment illustrates the solubility of carbonic dioxide in water, and one of the modes in which solutions of gases are prepared. (3.) If some lime-water is poured into a bottle of the gas, it will become cloudy, owing to the formation of an insoluble calcic carbonate. If this turbid solution is shaken up in another bottle of the gas, it will become clear. Lastly, if the clear liquid is heated to boiling, bubbles of carbonic dioxide will be given off, and a turbidity will again appear. The reason of this is, that there are two calcic

carbonates ; one insoluble in water, having the formula CaCO_3 , (ordinary chalk) ; the other soluble in water, having the formula $\text{CaH}_2(\text{CO}_3)_2$. This latter is formed in presence of an excess of carbonic dioxide, and is decomposed by boiling. The presence of much of the lime in spring-water, and the deposit or 'fur' formed in kettles in which such water is boiled, are thus accounted for. (4.) If a little infusion of litmus be poured into a jar of carbonic dioxide, it will be faintly reddened. If the liquid be then transferred to a flask or test-tube, and heated, it recovers its original blue tint, owing to the escape of the gas. (5.) Carbonic dioxide does not extinguish flame, for the same reason that nitrogen does—namely, by excluding oxygen—but exerts a positively prejudicial effect on combustion, so as to prevent its occurrence, even when there is as much oxygen present as would otherwise have supported flame. In illustration of this, a mixture may be made at the pneumatic trough of four volumes of carbonic dioxide with one of oxygen. If a lighted candle be plunged into this mixture, it will be at once extinguished, although the proportion of oxygen present is as great as that in atmospheric air. In like manner, if a lighted tallow candle with a long wick be introduced into carbonic dioxide, it will be totally extinguished, whereas in nitrogen the wick would have remained red-hot, and might have been fully kindled by being plunged into oxygen.

588. (6.) The density of carbonic dioxide admits of demonstration by a striking experiment. The weight of the gas is such, that it may be poured like a liquid from one vessel to another, and a candle may be extinguished by letting the gas fall on it. A jar quite full of the gas should be taken for this purpose, and slowly emptied by inclining it till it assumes a horizontal position close to a candle. The jar should not be emptied directly above the candle, which frequently makes the experiment fail, in consequence of allowance not being made for the impetus in a lateral or horizontal direction, communicated to the gas by the inversion of the jar. If the latter be held a little above, but at the same time to the one side of the flame, and then gently

turned over, the candle will not fail to be extinguished. The descent of the gas may be also followed by pouring it into a vessel containing a little lime-water, when the latter becomes chalky. Owing to the weight of carbonic dioxide, it may be most readily collected by displacement—the delivery-tube being arranged so as to lead it (not, as in the case of ammonia, to the upper part of an inverted bottle, but) to the bottom of a bottle standing on the table. The rise of the gas in the bottle may be shewn by lowering a lighted taper into the latter; but the bottle should not be considered full until a light held a little above the mouth is extinguished, shewing that the gas is overflowing.

589. (7.) The influence of carbonic dioxide on respiration does not admit of illustration by experiment unless by the cruel one of introducing a living animal into the gas, when it becomes insensible, and in a short time, if not removed, dies. Carbonic dioxide does not extinguish life by simply causing suffocation—that is, by cutting off oxygen, as nitrogen does, or water, when an animal is drowned in it. The first-mentioned gas is a positive poison, and occasions death though all the other conditions of life are fulfilled. Thus air containing a proportion of carbonic dioxide so comparatively small that it does not extinguish flame, will nevertheless, if long breathed, extinguish life. This fact cannot be too carefully remembered, as fatal accidents are constantly occurring from ignorance or neglect of it. During the cold season of the year, persons are often tempted to introduce braziers or pans of red-hot charcoal into their apartments. Such contrivances have not chimneys communicating with the outer air, so that the carbonic dioxide produced of necessity escapes into the room, and rapidly vitiates its atmosphere. Fuel should never be burned in rooms, unless in fireplaces provided with chimneys, and well ventilated, so that the products of combustion do not accumulate within the apartment.

590. The following experiments, throwing light on important relations of carbonic dioxide, should also be tried. The vinous fermentation, as already mentioned, is attended by the

production of carbonic dioxide. Those who can obtain access to a brewing-vat may have instructive evidence of this in several ways. A candle, let down into a tun containing fermenting beer, will be at once extinguished. A vessel containing lime-water, suspended within it, will soon exhibit the chalkiness characteristic of the action of carbonic dioxide. An infusion of litmus in the same circumstances will become faintly reddened.

591. On the small scale, a little brown sugar, water, and yeast may be placed together into a gas-bottle, such as that used for preparing hydrogen. If this be put in a warm place, gas will soon be evolved, which may be conducted by means of the delivering tube through lime-water, so as to obtain proof that it is carbonic dioxide. Or a little fresh beer may be placed in a retort, the beak of which dips into lime-water, and heat applied to the liquid. Carbonic dioxide will soon be evolved.

592. During animal respiration, carbonic dioxide is given off abundantly. In proof of this, it is only necessary to blow, by means of a tube, through lime-water, so that the air expired from the lungs may act upon it. A few minutes' blowing will cause a copious precipitate of calcium carbonate.

593. Whilst discussing the atmosphere, reference was made to the power of living green plants to decompose carbonic dioxide when shone upon by the sun. In proof of this, a recently cut branch, with healthy green leaves upon it, may be placed within a jar of carbonic dioxide standing over water, and the whole exposed to direct sunlight. Or the branch may be placed in a deflagrating jar filled with water partly saturated with carbonic dioxide, and the gas evolved may be collected in a test-tube fitted by a cork into the neck of the jar. After an interval, which will vary according to the brightness of the day, but may amount to one, two, or six hours, the gaseous contents of the jar, when examined, will be found to have lost all power to precipitate lime-water, and instead of extinguishing flame, will support it brilliantly. In short, the carbonic dioxide has been replaced by oxygen, in consequence of the

plant resolving the former into its constituents, and retaining within itself the carbon, leaving the oxygen free.

594. Analysis shews that the proportion of carbonic dioxide in the air varies very little from year to year, although it is constantly passing in large quantity into the atmosphere as a product of combustion, respiration, fermentation, volcanic action, &c. It is prevented from accumulating, so as to become fatal to animal life on the globe, by this remarkable action of plants, which not only withdraw the poisonous carbonic dioxide, but replace it by the vital oxygen.

595. The composition of carbonic dioxide may be ascertained either by analysis or synthesis.

(1.) When a known weight of carbon is burnt in oxygen (in an apparatus similar to fig. 50, page 195), and the carbonic dioxide collected and weighed, it is found that 12 grms. of carbon unite with 32 of oxygen to form 44 grms. of carbonic dioxide.

(2.) When a piece of magnesium wire is coiled into a spiral, heated until it burns in air, and then plunged into a jar of carbonic dioxide, it continues to burn in the gas, and a white powder, magnesian oxide, together with black flakes of carbon, are produced. This method, although not adapted for accurate analysis, is sufficient to demonstrate the presence of carbon in the gas.

(3.) Neither of the above processes gives any indication of the number of atoms of carbon and oxygen in the molecule of carbonic dioxide. But when the pure gas is transmitted through a red-hot iron tube, the iron deprives it of one-half of the oxygen it contains, and carbonic oxide is obtained. By this and other experiments, we learn that the oxygen can be taken out of it in two portions, while the carbon is taken out altogether, when it is taken out at all; and we conclude that a molecule of the gas contains 1 atom of carbon associated with 2 atoms of oxygen (see page 150).

CARBONIC OXIDE.

| | | | |
|---------------|---------|---------|---|
| | Symbol. | Weight. | 1 litre weighs 1.251 gm. Density = 0.967 " |
| Molecule..... | CO | 28 | |

COMPOSITION.

1 litre yields :

$\frac{1}{2}$ a litre of oxygen, weighing 0.715 gm.

$\frac{1}{2}$ a litre of carbon gas (?), " 0.536 "

596. Carbonic oxide does not occur as a natural product, but is known only as produced artificially.

597. *Preparation.*—One method of obtaining the gas has been alluded to above (par. 595), namely, to pass carbonic dioxide over red-hot iron. The reaction is represented by the following equation :



The volume of the gas, as implied in the equation, is not changed by the abstraction from it of half its oxygen.

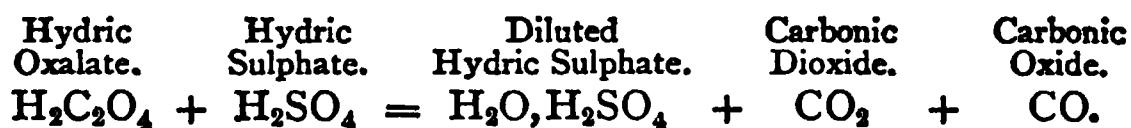
598. Carbonic dioxide may likewise be changed into carbonic oxide, by passing it through a porcelain tube containing red-hot charcoal. The carbonic dioxide combines with a second atom of carbon, and becomes carbonic oxide, thus :



Here 88 grms. of carbonic dioxide combine with 24 grms. of carbon, and form 112 grms. of carbonic oxide, the volume of the gas being doubled. This change is constantly occurring in charcoal and coke fires. At the lower and outer part of the chauffer or fireplace, the hot charcoal combining with the oxygen of the air, forms carbonic dioxide. Much of this ascends through the red-hot fuel in the body of the fireplace, and being thus exposed to a great excess of red-hot charcoal, combines with it, forming carbonic oxide : when this reaches the surface, it burns, producing carbonic dioxide. The flame of carbonic oxide is blue, but when seen against a ground of red-hot

cinders, it appears purple. It is matter of popular observation that the appearance of such a flame in the fireplace is an indication of frosty weather. A low temperature, such as that of 0° , favours the production of carbonic oxide in the way mentioned, by condensing nearly all the moisture in the atmosphere, so that our fires are maintained at that temperature by almost dry air.

599. For experimental purposes, carbonic oxide is not prepared in either of the ways mentioned. The deadly poison oxalic acid (hydric oxalate), which is sold in the shape of small white crystals, when heated in a retort along with strong hydric sulphate, yields a mixture of this gas and carbonic dioxide. The gas is not evolved till the temperature of the hydric sulphate has been raised considerably; but when the gas begins to come off, it is evolved with great rapidity, so that the jars intended to receive it should be standing full of water from the beginning of the process. The reaction may be expressed as follows :



600. In this way a mixture is obtained of carbonic dioxide

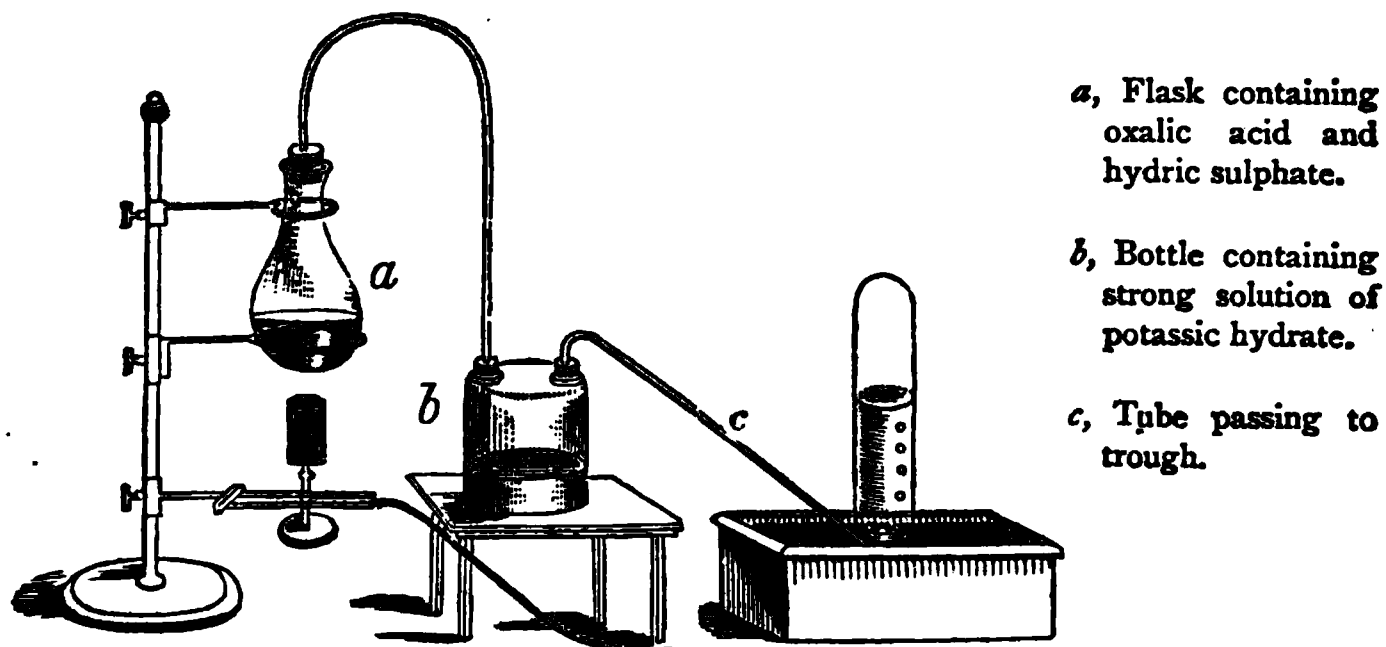


Fig. 57.

and carbonic oxide. By pouring into the gas-jars a small

quantity of lime-water or solution of potassic hydrate, the carbonic dioxide may be absorbed, and the carbonic oxide left; or the mixture of gases may be passed through a solution of potassic hydrate which retains the carbonic dioxide. Fig. 57 shews an arrangement which may be employed for this purpose.

601. A very good method of obtaining pure carbonic oxide is the following, devised by Professor Fownes. About 100 c.c. of strong hydric sulphate are placed in a flask, and 15 grms. of powdered potassic ferrocyanide (yellow prussiate of potass) are added by degrees. The mixture, when cautiously heated, gives off nearly pure carbonic oxide. The regulation of the heat is the only matter of difficulty: the lamp should be lowered, or temporarily withdrawn, as soon as any sign of effervescence appears.

602. *Properties.*—Carbonic oxide is a colourless, invisible gas, having a slight oppressive odour, and no taste. It does not support combustion nor respiration, nor does it, when pure, produce any precipitate in lime-water. It is one of the gases which have never been condensed to a liquid by any pressure we can command. One litre of water, at 15°, only dissolves 24 c.c. of the gas. It is more poisonous than carbonic dioxide, and is one of the causes of the fatal result which attends prolonged exposure to the fumes of burning charcoal. Its most striking property is its combustibility. It burns with a very beautiful blue flame, combining with the oxygen of the air, and forming carbonic dioxide, according to the following equation:



The pure gas, if mixed with half its volume of oxygen, and kindled, detonates sharply; and the production of carbonic dioxide may be proved in the usual way, by adding lime-water to the jar after the explosion.

Compounds of Carbon and Hydrogen (Hydrocarbons).

603. The compounds of carbon and hydrogen are not less interesting than those of carbon and oxygen. They are very

numerous, and occur alike as solids, liquids, and gases. We can refer, however, only to some of the more important of them, which are of more than ordinary theoretical and practical importance. They are, strictly speaking, organic compounds, but their consideration cannot be delayed till organic chemistry is discussed.

604. Coal-gas depends for its illuminating power on two gaseous compounds of carbon and hydrogen. Each of these is called *carburetted hydrogen*; but as the one of them is nearly twice as heavy as the other, they are distinguished by the names *light* and *heavy* carburetted hydrogen. They belong, however, to different organic series, and their modern names are ethylene and methylic hydride, respectively.

ETHYLENE.

| | Formula. | Weight. | |
|---------------|------------------------|---------|--|
| Molecule..... | H_4C_2 | 28 | 1 litre weighs 1.252 gm. Density = 0.979. |

COMPOSITION.

1 litre yields :

2 litres of hydrogen, weighing 0.1792 gm.

1 litre of carbon gas (?), " 1.073 "

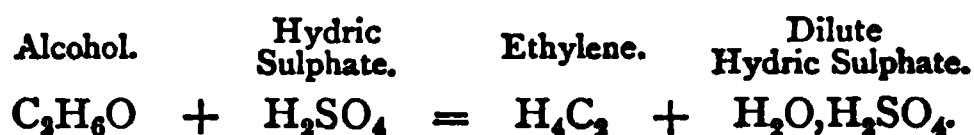
605. Ethylene is often called olefiant gas, a name which it derives from its property of forming an oily liquid when it combines with chlorine. Though heavy as a compound of carbon and hydrogen, it is light when compared with other gases. Air being the standard of density, only those gases which are denser than it are called heavy. Olefiant gas, however, is lighter in the proportion of .978 to 1.000.

606. This gas is obtained by placing in a retort, or in a flask such as was used for preparing hydrogen (fig. 40), a mixture of 50 c.c. of ordinary alcohol (rectified spirits of wine) with 100 c.c. of strong hydric sulphate.* A little sand should be added, to lessen the tendency to froth up towards the end of the

* The mixture should be made beforehand, and the acid should be gradually added to the alcohol, not *vice versa*. Much heat is evolved, and it is well to place the vessel in a dish, in case it should break.

action. Heat is then applied, and in a short time the liquid grows dark, and evolves olefiant gas with great rapidity. It may be collected at the pneumatic trough in the usual way. Its production depends on the following change.

607. Alcohol may be represented as containing the elements of one molecule of ethylene, and one molecule of water. When heated with excess of hydric sulphate, the latter combines with the water, and the ethylene is evolved. Thus :

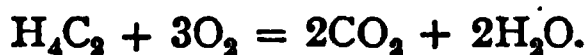


608. *Properties.*—Ethylene is colourless and invisible, scarcely soluble in water, and does not support combustion or respiration. The most striking property of this gas is its combustibility. It burns with a dense bright flame, producing, during its combustion, carbonic dioxide and water, from the combination of its carbon and hydrogen with the oxygen of the air.

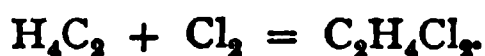
609. The following experiments may be tried with it :

(1.) A jar of the gas kindled will enable its combustibility and the brightness of its flame to be witnessed. This is a point of interest, as the illuminating power of coal-gas is in great part dependent on the presence in it of ethylene.

(2.) A strong thick jar is to be filled one-fourth full of the gas, and the remaining three-fourths with oxygen. When a light is applied to this mixture, it occasions a loud and powerful explosion, accompanied by the evolution of much heat, but little light.

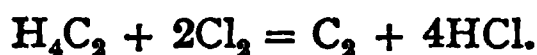


(3.) A jar half-full of chlorine gas is to be placed on the stool of the pneumatic trough, and filled up with olefiant gas. The gases will rapidly unite, combining to form a liquid, which will be seen collecting like drops of oil on the surface of the water which ascends within the jar. This experiment illustrates the origin of the name *olefiant*.



The substance represented by the formula $C_2H_4Cl_2$ is called ethylenic dichloride. Its original name was 'Dutch liquid,' from its discovery by some Dutch chemists.

(4.) A similar mixture of one measure of olefiant gas and two of chlorine may have a light applied to it, when it will burn with a smoky flame, and deposit within the jar a large amount of soot. This phenomenon results from the chlorine combining with the hydrogen of the olefiant gas, and rejecting the carbon, the presence of which in the invisible carburetted hydrogen is thus demonstrated. The equation expressing the change is :



610. When Dutch liquid is subjected to the continued action of chlorine, a series of compounds is obtained, the hydrogen of ethylene being replaced by chlorine in four successive instalments. This fact, which was discovered by Faraday, leads us to believe that the molecule of ethylene contains 4 atoms of hydrogen.

METHYLIC HYDRIDE (MARSH-GAS).

| | Formula. | Weight. | |
|---------------|----------|---------|---|
| Molecule..... | H_4C | 16 | 1 litre weighs 0.715 grm. Density = 0.553. |

COMPOSITION.

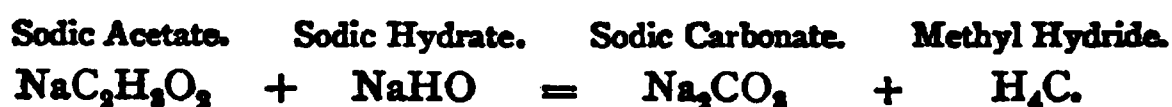
1 litre yields :

2 litres of hydrogen, weighing 0.1792 grm.
 $\frac{1}{2}$ a litre of carbon gas (?), " 0.536 "

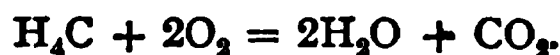
611. This compound is best known as a natural product, being the gas which issues from the ground in various parts of the world, and admits of being kindled. Stagnant water in which vegetable matter is decaying gives off this gas, mixed with carbonic dioxide. Hence its name *marsh-gas*. It also issues as a product of decomposition from beds of coal, and when it mingles with air, forms the explosive mixture which leads to so many destructive accidents in our coal-pits. It has been called by the miners *fire-damp*.

612. It can be prepared artificially by strongly heating a

mixture of 40 grms. crystallised sodic acetate, 40 grms. solid potassic or sodic hydrate, and 60 grms. of quick-lime in powder. The gas is evolved in great abundance, and can be collected over water. The heat required is high, and it is best to use a flask of very infusible glass, such as a Florence flask. The reaction is a complex one, and can hardly be understood without reference to organic chemistry. The equation expressing it is :



613. *Properties.*—Methyl hydride is a colourless, invisible, inodorous gas, scarcely soluble in water, which does not support combustion or respiration, but is not poisonous. It has never been liquefied by cold or pressure. It burns with a white flame, but has not so great an illuminating power as olefiant gas. The only experiment that admits of being tried with it is the action of flame on it when mixed with oxygen or air. If mingled with twice its volume of oxygen, or ten times its volume of air, it detonates powerfully, and water and carbonic dioxide are produced.



614. The molecule of methylic hydride is believed to contain 4 atoms of hydrogen in combination with 1 atom of carbon, for reasons which would not be clear without a reference to organic chemistry. It may, however, be said that there are indications of our being able to take out the hydrogen in four instalments (compare what has been said of ethylene, par. 610), while the carbon does not seem to be divisible.

COAL-GAS.

615. Coal-gas is not a definite chemical compound, but a mixture of many unlike substances, obtained by exposing coal to a red heat in gas (clay or iron) retorts. The coal preferred for this purpose is cannel coal, the bright shining variety which does not soil the fingers. When heated in a retort, it yields a

variety of products, among which three are specially important :
1st, Tar, a highly complex mixture of various compounds of carbon and hydrogen. *2d*, Ammonic carbonate and sulphide. *3d*, Ethylene and methylic hydride. Besides these, there are variable quantities of hydrogen, nitrogen, carbonic oxide, carbonic dioxide, hydric sulphide (sulphuretted hydrogen), &c.

616. The gas, as it issues from the retorts, is received into a large horizontal iron chamber, half full of liquid, and from thence passes through a series of large iron siphons, kept cool, in which it deposits the tar and ammoniacal liquor. The gas is then made to traverse vessels containing slaked lime, or through a chamber with dry lime. The lime absorbs the useless carbonic dioxide and noxious sulphuretted hydrogen (the latter being more effectually separated by passing the gas over trays containing ferric oxide), and the gas is then collected in large metallic reservoirs, from which the pipes which distribute it proceed. Ordinary coal-gas, in spite of the purification to which it is subjected, contains a variable amount of different substances, some of which are of no service, and others are positively prejudicial. The hydrocarbons are the only valuable constituents of coal-gas, so far as its application to the production of light is concerned. The composition of a sample of coal-gas is given below.

| 100 litres contain : | |
|---|--------------|
| Hydrogen | 45.6 litres. |
| Marsh-gas..... | 35.0 " |
| Ethylene..... | 4.6 " |
| Carbonic Oxide..... | 7.4 " |
| Carbonic Dioxide..... | 3.7 " |
| Nitrogen..... | 3.5 " |
| Hydric Sulphide, and traces of other gases..... | 0.2 " |
| | <hr/> |
| | 100.0 " |

DAVY LAMP.

617. The dangerous explosions which occur when a light is applied to a mixture of fire-damp and air, have already been referred to, but the discussion of the methods by which, on the

large scale, they may be prevented, has been postponed till the nature of coal-gas should have been made known, because the experiments we are about to mention can be much more conveniently tried with coal-gas, of which fire-damp is the chief constituent, than with fire-damp itself.

618. To prevent accidents in coal-pits, Sir Humphry Davy devised a very ingenious lamp, which goes by the name of the Davy or Safety Lamp, and is intended to furnish the miner with a source of light which shall have no power to kindle fire-damp.

619. Fire-damp alone does not burn or explode. It must be mingled with air before either of these phenomena can shew itself. If, however, it be mixed with too much air, explosiveness is again lost. Detonation occurs most powerfully when the fire-damp is mixed with from eight to ten times its volume of air. If the proportion of air be diminished to three or four times that of the fire-damp, or be increased to more than fourteen times its measure, explosion does not happen. Where the volume of air is very small, an amount of oxygen sufficient to burn the fire-damp is not furnished. Where the quantity of air, on the other hand, is too large, it prevents the spread of flame by conducting away heat, and preventing the temperature rising high enough to inflame the combustible gas.

620. The fact last referred to is taken advantage of in the construction of the Davy lamp. Fire-damp cannot be kindled unless it be raised to a white heat, unlike pure hydrogen, which takes fire at the lowest visible red heat. When an explosive mixture, accordingly, collects in a coal-mine, in consequence of the fire-damp issuing from the seams of coal, and mingling with the air, if it meets a naked flame, such as that of a candle which is at a white heat, explosion at once happens. The object of the Davy lamp is to enable the miner to employ artificial light in the midst of such an explosive atmosphere without any risk of kindling it. This is done in the following way: The safety lamp consists of a small cylindrical oil-lamp, differing in no respect from those in ordinary use, except that a brass

wire passes through a canal traversing the lamp from below, and is bent over close to the wick where it issues at its surface, so that by turning this wire, the wick can, to a certain extent, be trimmed without uncovering it (see fig. 58). The peculiarity of the lamp consists in a cover or cage of wire-gauze, which is screwed on to the top of the lamp after the wick is lighted. This wire-gauze cover is made double at the top, for the sake of strength, but a single layer of the gauze, so long as it is entire, renders the lamp quite safe in an explosive atmosphere.



Fig. 58.

621. When the lamp, as we have described it, is carried into an explosive mixture of fire-damp and air, no explosion happens. The mixture of gases traverses the apertures in the gauze, and burns around the wick, but the flame does not travel *outwards* through the meshes of the wirework, so as to kindle the mass of fire-damp without. The lamp makes explosion impossible, not, as is often imagined, by preventing the fire-damp reaching the flame within the cage, but by preventing that flame from reaching the fire-damp without. The light is put out whilst in the very act of traversing the wire-gauze, in consequence of the latter, which is an excellent conductor of heat, carrying that away, and so causing the temperature of the flame to fall below the white heat necessary for kindling fire-damp.

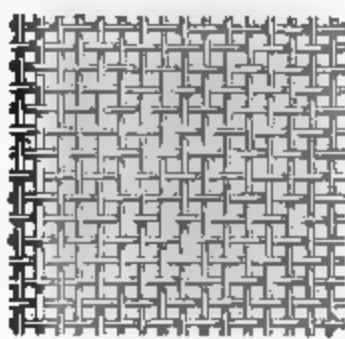


Fig. 59.

622. A piece of wire-gauze, in truth, consists essentially of a multitude of metallic tubes, or canals, placed side by side (see fig. 59). These tubes are exceedingly short, so that we are apt to forget that they are tubes at all; but canals they certainly are, with walls, comparatively speaking, very thick, and consisting of a metal, one of the best conductors of heat. In the Davy lamp, as

we have described it, the flame is at one end of each of these metallic tubes, and the mass of explosive mixture ready to be fired is at its other extremity. The tube, too, is filled with the explosive mixture, which, like a train of gunpowder, must be kindled, otherwise the flame will not be propagated through the tube. The flame, however, never can succeed in traversing the canal, for a portion of the explosive mixture set fire to at one end of it is unable to kindle the portion lying next it in the canal, in consequence of the sides of that canal absorbing the heat, and thus cooling the mixture of gas and air below the point at which they combine.

623. The following simple experiments will illustrate the facts just explained :

- (1.) A small metallic spiral may be formed by coiling iron wire round a pencil (fig. 60). If this be

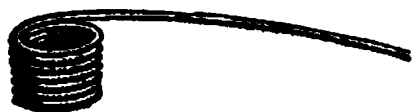


Fig. 60.

gently placed, like an extinguisher, over the wick of a burning candle, which it should be large enough not to touch, the light will go out ; the burning vapour of

the wax or tallow being unable to maintain itself at a white heat when in contact with a mass of metal.

- (2.) A piece of wire-gauze is to be pressed down on the flame of a candle, or, still better, on a jet of burning gas (fig. 61).

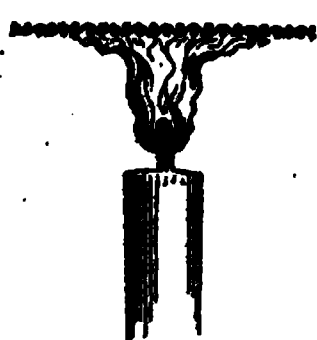


Fig. 61.

It will be found to intercept the flame, which will burn only on the lower side of the gauze.

(3.) That the gauze acts by arresting the flame, not by stopping the passage of the gas, may be proved by pressing the wire-gauze over a gas-flame, and then applying a lighted match to the upper surface. It will set fire to a volume of combustible gas, which has all the while been ascending through the meshes of the wirework, but which the flame below was unable to kindle.

- (4.) A still more striking experiment is to lay the wire-gauze on a nozzle from which coal-gas is issuing, and then to light the gas on the upper surface of the wirework. If the gauze be

then raised gently, it may be lifted to the extent of 8 or 10 cm. above the nozzle, carrying a tongue of flame with it, fed by a column of gas ascending from the nozzle, but which is not kindled by the burning gas above.

(5.) A piece of camphor may be laid on a sheet of wire-gauze and kindled. It will burn with a dark, smoky flame, at the same time melting, and dropping through the gauze. But though the drops are as combustible on the lower as on the upper surface of the wirework, the flame will not descend through the meshes, or kindle the melted camphor below.

(6.) For the following experiment, a Davy lamp, if it can be procured, should be employed. In the absence of it, a cylindrical cage may be constructed of wire-gauze, and laid over a lighted candle, or an oil or spirit lamp. A jet of coal-gas is now to be directed, by means of a flexible tube, against the cage, so as to pass through its meshes, and reach the flame. It will take fire and burn within the cylinder, but the extremity of the flexible tube may be pressed close against the wire-gauze without the flame being communicated to the jet of gas. If the stream be made to envelop the flame of the lamp in large quantity, the light will go out, in consequence of the exclusion of air; a phenomenon occasionally witnessed in coal-pits, but forming no essential objection to the value of the lamp, as it is only witnessed when the volume of fire-damp is so large that the atmosphere of the pit is irrespirable.

624. The Davy lamp appears to afford a complete protection against explosion, except where a very rapid current of fire-damp, issuing, as it frequently does, with great force from cavities in the coal where it has been pent up, impinges against the lamp. In these circumstances, it may hurry the burning gas so swiftly through the wire-gauze, that the latter has not time to lower its temperature below the explosive point.

625. When an explosion happens in a coal-pit, much carbonic dioxide is produced, along with water, in consequence of the carbon and hydrogen of the fire-damp combining with the

oxygen of the air. This carbonic dioxide is called by the miners the 'after-damp,' or 'choke-damp;' and it is as great a cause of mortality at an explosion as the mere mechanical violence occasioned by the detonation.

STRUCTURE OF FLAME.

626. The artificial lights which we employ—such as lamps, candles, and gas-flames—all owe their luminosity to the combustion of compounds of carbon and hydrogen. It is convenient here, accordingly, to discuss the nature of flame, the cause of its luminosity, and the chemical principles involved in the construction and employment of the blow-pipe.

627. By the word flame, we denote gas or vapour raised to so high a temperature that it emits light as well as heat. All flames are not equally hot, but their temperature is always high, and when at its maximum, exceeds that of solid bodies at an ordinary white heat.

628. The flame of a lamp, or candle, or simple gas jet, consists of a hollow cone, in the centre of which there is no combustion. If one of these flames, especially that of a candle, which illustrates the phenomena best, be examined closely, it will be seen to have a triple structure. Directly above the wick, a dark or non-luminous space is visible. This is surrounded by a shining envelope, or luminous cone, which deposits soot upon a cold body introduced into it. External to this, a second cone may with difficulty be traced, having far less luminosity than the first, but possessing a very high temperature.

629. The central space appears dark only by contrast with the luminous cone which surrounds it. It consists, in reality, of transparent, invisible compounds of carbon and hydrogen, which are constantly rising in vapour from the wick. This may be proved in two ways: (1.) If a glass tube, open at both ends, be held obliquely in the flame of a candle, with its lower extremity in the dark central space above the wick, it will conduct away much of the combustile vapour, which may be

kindled at its upper end in the way shewn in the accompanying figure (fig. 62). (2.) If a piece of fine wire-gauze be pressed down on the candle-flame, and this be looked at from above, through the gauze, whilst combustion is going on only below, the flame will appear like the mouth of a tube, the walls of which are luminous. The unburned gas which occupies the centre, and, as it were, fills the luminous tube, rises through the

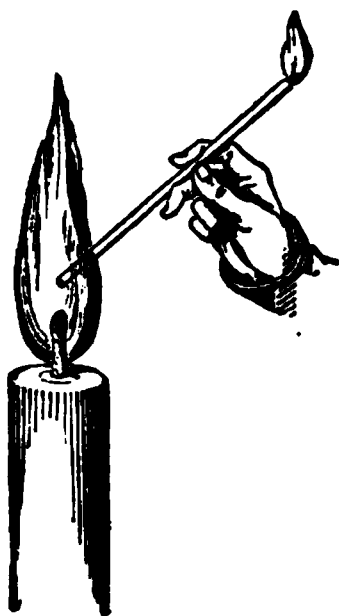


Fig. 62.

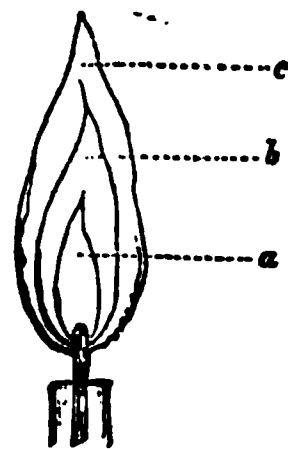


Fig. 63.

a, Area of no combustion.
b, Area of partial combustion.
c, Area of complete combustion.

wire-gauze, and, as mentioned under the Davy lamp, may be kindled at its upper surface. If, moreover, a lighted candle be held between the eye of the observer and a sheet of paper or other white object, the latter will be seen through the apparently dark central space (fig. 63). This flameless portion of the flame may be distinguished by the title of *the area of no combustion*.

630. The luminous cone which envelops the dark space is characterised as *the area of partial combustion*. In it a limited amount of oxidation occurs, in virtue of the oxygen of the air penetrating to that depth, so as to combine with the hydrogen and carbon; but the amount of oxygen which does reach these combustibles is not sufficient to oxidise both, and is almost entirely spent in converting the hydrogen into water.

631. The outer cone is named *the area of complete combustion*,

because in it the entire oxidation of the carbon is effected ; and as a result of this, a high temperature is produced.

632. These three areas are not sharply marked off by visible lines of demarcation, but, on the other hand, shade away into each other ; and in the case of a simple combustible gas, such as hydrogen, we pass by imperceptible gradations from the central space of no combustion to the outer one of complete oxidation. In the flame, however, of gaseous hydrocarbons an additional phenomenon appears, which accounts for the highly illuminating power of compounds of this class, as compared with the simple combustible gases. Oxygen has a much greater affinity for hydrogen than for carbon ; so that, when presented in small quantity to a compound of carbon and hydrogen, it is entirely (or almost entirely) spent in oxidising the hydrogen, whilst the carbon separates in the solid form. This is the cause of the deposition of soot on bodies introduced within the inner luminous cone, and is taken advantage of, as we have mentioned already, in the preparation of lampblack. It accounts also for the great illuminating power of the area of partial combustion. Its luminosity results from the fact, that whilst the hydrogen only of the combustible is burned by the oxygen of the air which penetrates to that depth, the high temperature produced by the burning hydrogen raises to a white heat the solid, unburned carbon, which, like the lime in the lime-ball light, is the true source of the brightness of the flame. In the outer area the white-hot carbon meets abundance of oxygen, and combining with it, raises the temperature of the surrounding air to some considerable distance from the visible flame.

633. The highly illuminating power of compounds of carbon and hydrogen is thus traced to the fact that their hydrogen and carbon do not burn simultaneously, but successively, and in such a way that the one heats the other white-hot. It is quite possible to make them burn contemporaneously ; but when they do, the light they evolve is extremely feeble, not greater, indeed, than that of pure hydrogen. Thus

elefant gas and light carburetted hydrogen, which, when kindled at a jet or the mouth of a jar, burn with highly luminous flames, exhibit scarcely any luminosity when detonated with the proper proportion of air or oxygen. In the latter case, the carbon burns as fast as the hydrogen.

634. The same fact may be illustrated very simply with coal-gas, by placing over a jet from which it is issuing a chimney or hollow cylinder, covered at the top with wire-gauze. When the gas is turned on, it ascends within the chimney, and mixes with air before passing through the gauze. By a little adjustment of the stop-cock, the gas may be supplied in such quantity that it shall be mixed with enough of air to oxidise, when it is kindled, both its carbon and hydrogen. On lighting it above the wire-gauze, it burns with a pale-blue flame somewhat like that of carbonic oxide, and not more illuminating.

635. The Bunsen burner, one of the most useful forms of burner ever invented, is constructed on the same principle. It consists of a piece of brass tube about 1 cm. in diameter, and 12 or 14 cm. in height, fixed on an iron base (fig. 64). Near the bottom of this tube several holes are pierced. The gas enters through a flattened jet, which terminates just above the holes, and, as it rises in the tube, mixes with the air which enters through the holes. When a light is applied to this mixture of gas and air as it issues from the top of the tube, it burns steadily without descending in the tube, so long as the current of gas is uniform, and the supply of air not too great. The tube, in fact, represents one of the meshes of the wire-gauze, and cools down the mixture of gas and air within it. The flame of this burner is smokeless, depositing no soot on substances held in it; and its temperature is very high, approaching that of the blow-pipe flame. By enclosing it within a fire-clay cylinder, its heating effects are much increased, and even iron may be melted in a furnace constructed by Messrs Griffin on this principle.

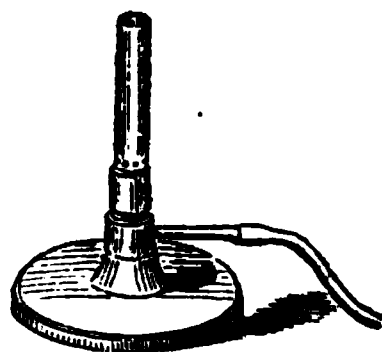


Fig. 64.

636. From these experiments, it appears that it is not the mere presence of carbon in coal-gas, or in oil or tallow, that makes their flames luminous, but the fact that the carbon in a solid state is heated white-hot during their combustion. All highly luminous flames, indeed, contain white-hot *solid* matter. The lime-ball light furnishes evidence of the converse of this—namely, that the most feebly luminous flame may be rendered highly illuminating by introducing within it a solid which it may heat.

637. In further evidence of this, it may be noticed that where a combustible, as well as the product of its combustion in air or oxygen, is a *solid*, much light is always evolved; but where the inflammable and its oxide are gases, or liquids, the flame is very feeble. Thus iron burned in oxygen, and the metals generally, when undergoing rapid oxidation, are highly luminous; for the metals are solids, and their oxides are also solids. For the same reason, solid phosphorus, which forms solid phosphoric acid when it burns, evolves an intense light; but sulphur, which, though solid, yields, when burned, a gas (sulphurous anhydride, SO_2), is but feebly luminous; and hydrogen gas, the product of whose combustion is also a gas, or vapour, H_2O , is still less illuminating.

THE BLOW-PIPE.

638. The blow-pipe (figs. 65 and 66) consists simply of a glass or metallic tube, with a mouth-piece (*a*) at one extremity, and a nozzle (*b*) of small bore at the other, through which a stream of air can be forced across the flame of a lamp or candle (fig. 67). By means of it air is furnished to what in an ordinary upright flame is the central area of no combustion, so that oxidation goes on both in the centre of the flame and along its outer border.

639. When the blow-pipe flame is examined, it is seen to consist of two elongated cones, the inner blue, the outer pale yellow. Between these cones there is a space, corresponding

in some measure to the middle area of partial combustion

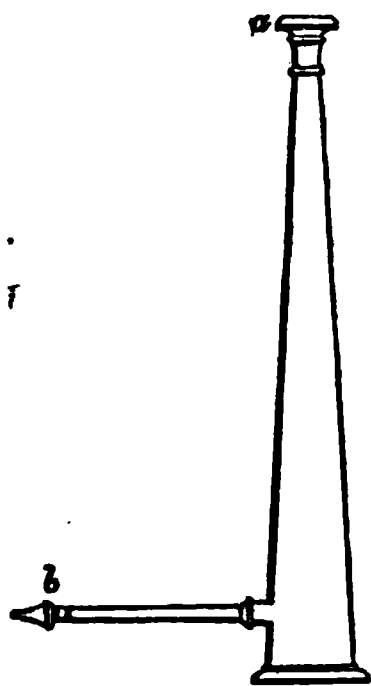


Fig. 65.



Fig. 66.

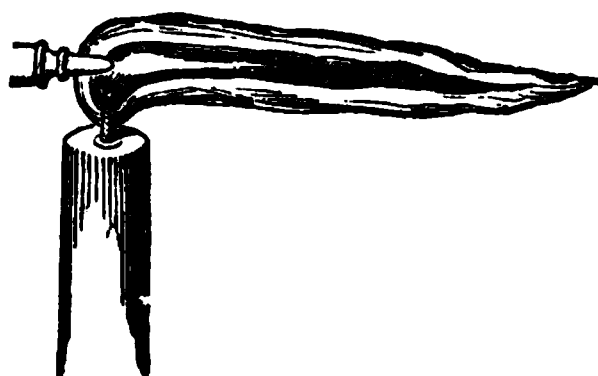


Fig. 67.

of an upright flame, but at a much higher temperature. This is distinguished as the *reducing* portion of the flame, or, more briefly, as the *reducing flame* of the blow-pipe; because the large amount of white-hot carbon which it contains enables it to reduce—that is, deprive of oxygen—the great majority of metallic oxides, so that their oxygen forms carbonic dioxide, and the metal separates.

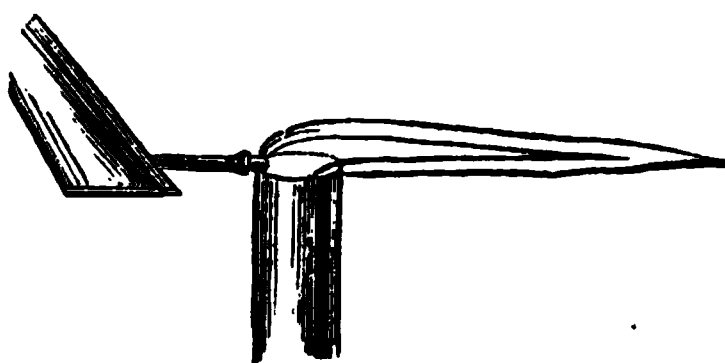


Fig. 68.

640. The tip or point of the outer pale-yellowish cone, and to a certain extent its whole external border, is called the *oxidising* flame of the blow-pipe; because metals, and other easily oxidised bodies, are rapidly converted into oxides when held in this portion of the flame, in consequence of the high temperature to which it elevates the air immediately in contact with it. The term *oxidising flame*, in truth, is not strictly correct; for it is the heated air, and not the luminous flame, which produces the oxidation; and bodies must be held a little in front of the visible flame in order to secure their oxidation.

641. For use with the blow-pipe, the flame of a common candle will answer; the jet being so held that the wick may not interfere with the stream of air. A Bunsen burner, arranged to give a luminous flame, by stopping up the air-holes at the bottom of the tube, may be used. But the best form of burner is that shewn in fig. 69. It is made from a short piece of brass tube, about 1 cm. in diameter, which is pinched at one end until a narrow slit is formed, through which the gas issues. The stream of air is to be directed through the flame, parallel to the slit, and thus the flame is more completely deflected than if the aperture were round.



Fig. 69.

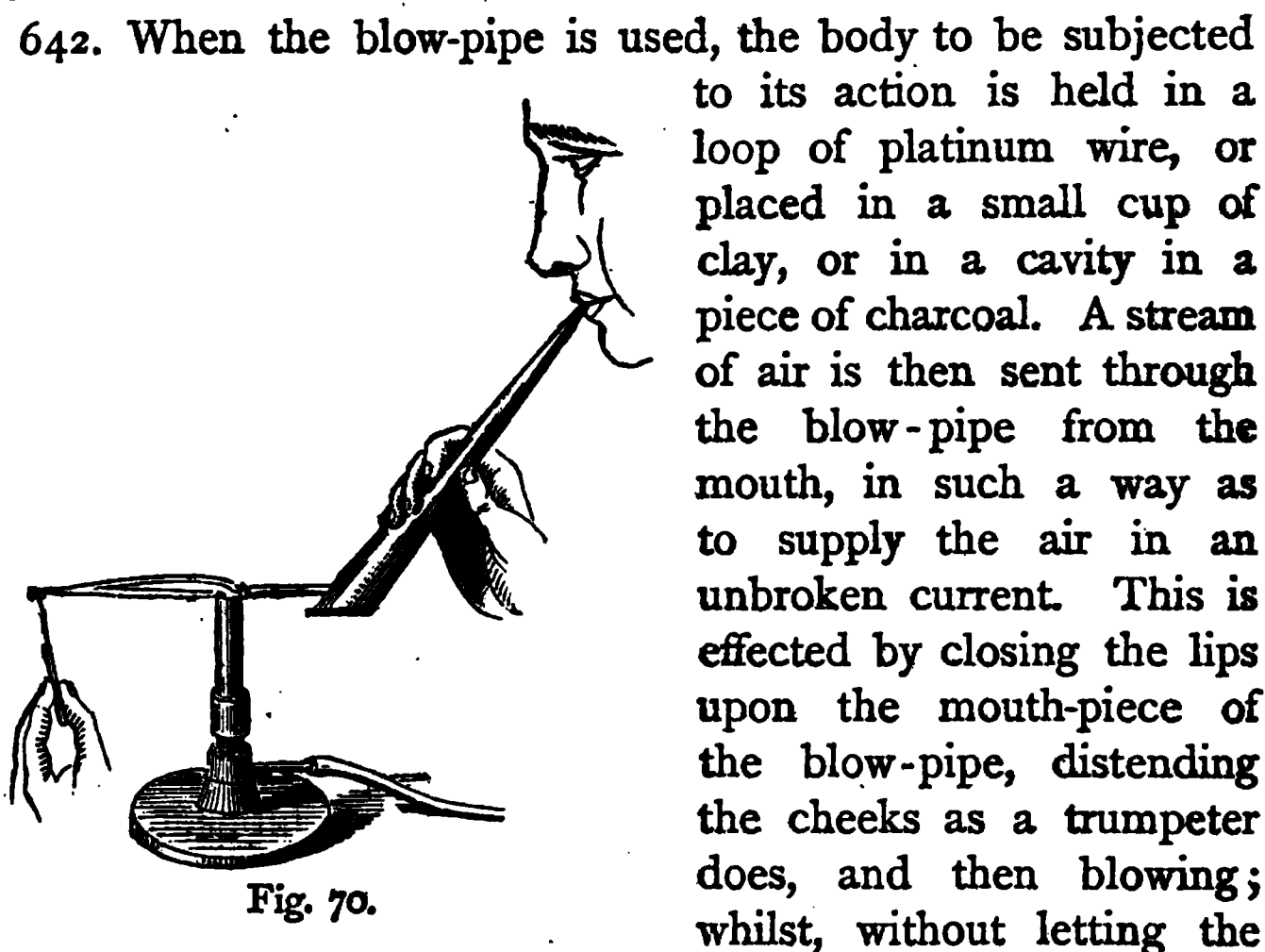


Fig. 70.

to its action is held in a loop of platinum wire, or placed in a small cup of clay, or in a cavity in a piece of charcoal. A stream of air is then sent through the blow-pipe from the mouth, in such a way as to supply the air in an unbroken current. This is effected by closing the lips upon the mouth-piece of the blow-pipe, distending the cheeks as a trumpeter does, and then blowing; whilst, without letting the cheeks collapse, air is simultaneously, or at short intervals, drawn through the nostrils.

643. The method of blowing is easily learned. The beginner fails for a time, in consequence of supplying the current direct from his lungs, the quantity of available air in which is soon exhausted, so that the stream intermits, and the blower is out of breath. To secure an unbroken stream, air must at the

same time be drawn in by the nostrils, so as to maintain respiration, and be expelled by the mouth to feed the current. The cavity of the mouth is kept distended, to act as a reservoir, like the sack of a bagpipe, whilst, by a slight compressing action of the muscles of the cheeks, partially diminishing the capacity of that reservoir, the air is propelled along the blow-pipe.

644. In learning the use of this instrument, the beginner should not blow fiercely. It is continuity, not rapidity, of current that is chiefly desired; and as soon as he can blow, however gently, and at the same time take a breath by the nostrils, he has mastered the whole difficulty of the blow-pipe.

645. From what has been stated as to the structure of the blow-pipe flame, it will be understood that it makes the greatest possible difference as to the effect it produces upon any body introduced into it whether that substance be exposed to the reducing or the oxidising flames. These flames may be distinguished, as already mentioned, by their colours, the reducing flame being blue, and the oxidising yellow; but the inexperienced manipulator will not be able to produce the flames sharply defined from each other, so as to be able to recognise them by the difference in their tints. The following directions may assist the beginner in producing the most effective flame.

(1.) To obtain the highest possible temperature: The stream of air should be moderately strong, in order that as much gas may be burned as possible, and the substance should be held just at the tip of the blue cone, where the combustion is most complete.

(2.) To effect reduction: More gas and less air will be needed, the object being to burn the gas only partially, and thus to compel it to obtain oxygen from the substance submitted to its action. The stream of air should be gentle, so as to deflect the flame in the form of a long luminous tongue, within the tip of which the substance must be held, wholly immersed in the flame.

(3.) To effect oxidation: More air and less gas must be used,

the object being to provide an excess of highly heated oxygen to act upon the substance. The latter should be held about 1 cm. in front of the tip of the blue cone.

646. In illustration of the opposite powers of the blow-pipe flames, the student may place a fragment of metallic lead on a piece of charcoal, and expose it to the oxidising flame. The lead will rapidly become converted into its protoxide, litharge, and melt into a transparent globule. If this be now carried back within the flame, so as to be exposed to its reducing portion, the oxygen will be rapidly removed, and the lead reappear in its metallic state. This oxidation and deoxidation may be obtained alternately with the same piece of metal any number of times, and the reduction will be much assisted by the addition of a minute fragment of potassic cyanide.

647. In like manner, if a piece of white flint-glass be exposed to the reducing flame, the oxide of lead which it contains is deprived of its oxygen, and the glass acquires a brilliant, black, metallic coating, which renders it opaque. It may be rendered transparent again by exposing it to the oxidising flame.

648. Experiments similar to those first mentioned may be made with other metals besides lead—such as tin, zinc, bismuth, antimony; but none of them do so well as lead.

649. Another mode of experimenting with the blow-pipe may be illustrated as follows: A ring, about 2 mm. in diameter, is to be made at the end of a piece of platinum wire, by bending it round the tip of the blow-pipe nozzle, or otherwise. The ring is then to be heated and dipped, while hot, into powdered borax. The salt, when held in the hottest part of the blow-pipe, will give off water, and finally melt into a transparent glass-like bead. This borax-glass has the property of combining with many metals, in presence of oxygen, the resulting compound being often of a characteristic colour. Thus, if the bead is moistened with solution of a cobalt salt and again heated, it will acquire a beautiful blue tint, whether held in the oxidising or in the reducing flame. If a manganese salt is taken instead of cobalt, a bead will be obtained which is amethyst-red in the

oxidising flame, but loses its colour entirely when held for a short time in the reducing flame. Other instances will be alluded to under the different metals.

Compound of Carbon and Nitrogen.

CYANOGEN.

| | Formula. | Weight. | |
|---------------|--|---------|--|
| Atom..... | CN, or Cy | 26 | 1 litre weighs 2.329 grms. Density = 1.806. |
| Molecule..... | (CN) ₂ , or Cy ₂ | 52 | |

COMPOSITION.

1 litre yields :

1 litre of nitrogen, weighing 1.256 grm.
1 litre of carbon gas (?), " 1.073 "

650. While a full account of the compounds of cyanogen is more appropriately given under the head of Organic Chemistry, the substance itself has the same claims as ethylene and marsh-gas to be mentioned here. It has, moreover, this special interest, that it was the first substance isolated and examined which was recognised to be a compound radicle (see par. 317, page 123). It was discovered by Gay-Lussac in 1715. Its name is derived from two Greek words signifying to produce blue—in allusion to its being one of the ingredients in the paint Prussian blue.

651. Carbon and nitrogen cannot be made to combine directly, but when nitrogen is passed through a tube containing a mixture of carbon and potassic carbonate heated to redness, a salt is obtained containing 1 atom of potassium united with 1 atom of carbon and 1 atom of nitrogen, and called potassic cyanide :



This salt is practically obtained on the large scale in the following way : When parings of horns, skins, and other kinds of animal refuse are strongly heated with potassic carbonate (pearl-ash) and iron filings, the fused mass, when digested in

boiling water, gives a solution which yields bright yellow crystals on evaporation. This salt is the common 'prussiate of potass' (potassic ferrocyanide), and its composition may be represented by the following formula, $K_4Fe(CN)_6$. When it is heated in a covered crucible, it is decomposed into potassic cyanide, nitrogen, and a compound of carbon and iron, and the potassic cyanide can be dissolved out of the residue by water. This potassic cyanide is the chief source of cyanogen itself and its compounds.

652. *Preparation.*—When potassic cyanide and argentic (silver) nitrate, in the proportions of 6.5 parts of the former and 17 parts of the latter salt, are separately dissolved in water, and the solutions mixed, a white curdy precipitate of argentic cyanide is produced. This substance, when dried and heated in a test-tube, gives off cyanogen gas. Mercuric cyanide may be used instead of argentic cyanide. It is advisable not to collect any of the gas, since it is extremely poisonous, and its properties can be sufficiently examined as it issues from the mouth of the tube.

653. Cyanogen is a colourless gas, with a peculiar odour like that of peach-kernels. It is very soluble in water, and must therefore be collected over mercury. It is combustible, burning with a beautiful purple flame, with formation of carbonic dioxide and nitrogen:



The gas may be condensed into a colourless liquid by a pressure of about 4 atmospheres at ordinary temperatures, and frozen into a solid by a cold represented by -30° . It is very poisonous, and great care must be taken in experimenting with it.

654. Cyanogen forms a series of compounds with metals (potassium, for instance, may be burned in the gas), which are called cyanides, and which resemble chlorides in their constitution—the compound radicle, cyanogen (CN), replacing the simple radicle, chlorine (Cl), atom for atom. The properties of one of the most important of these, hydric cyanide, will be

considered next, together with the means of detecting cyanogen in combination.

HYDRIC CYANIDE (PRUSSIC ACID).

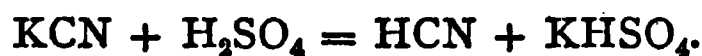
| | Formula. | Weight. | |
|---------------|----------|---------|--|
| Molecule..... | HCN | 27 | 1 litre weighs 1.208 gm. Density = 0.947. |

COMPOSITION.

1 litre yields :

| | |
|--|---------------------|
| $\frac{1}{2}$ a litre of hydrogen, | weighing 0.0448 gm. |
| $\frac{1}{2}$ a litre of nitrogen, | " 0.628 " |
| $\frac{1}{2}$ a litre of carbon gas (?), | " 0.536 " |

655. *Preparation.*—Hydric cyanide may be obtained in solution by distilling a mixture of potassic cyanide (or ferrocyanide) with diluted hydric sulphate. A good condensing arrangement is required, as the substance is very volatile. The reaction is similar to that by which hydric nitrate is obtained (par. 534), and may be thus represented :



If it is required in a pure anhydrous condition, the hydric sulphate must be less diluted, and the liquid which comes over must be shaken with calcic chloride, and redistilled. But the anhydrous acid is so formidable a poison (a single drop of it sufficing to occasion instant death), and its vapour is so volatile, that it should on no account be prepared in its state of greatest concentration, especially in a private dwelling. All its properties can be sufficiently examined with the diluted acid.

656. Anhydrous hydric cyanide is a colourless, limpid liquid, boiling at the comparatively low temperature of 26° , so that it is scarcely possible in summer to preserve it as a liquid. Its vapour occasions, even in small quantity, headache and faintness; and would cause death if largely inspired. It has a powerful, peculiar odour, generally compared to that of the peach blossom or of bitter-almond oil; its taste is pungent and cooling, but not sour. It must be observed with the acid only after it has been very much diluted. The necessity for the latter precaution will

be understood from the fact, that the strongest medicinal acid used in Great Britain does not contain in a hundred grammes more than three grammes of the pure or anhydrous prussic acid, and of this diluted acid a drop is a dose, which must be given warily. Hydric cyanide, in truth, must be prepared and handled very cautiously. It should not be placed in unlabelled bottles, or indeed kept in private dwellings. One of the most efficacious antidotes to poisoning with prussic acid is the affusion of cold water, such as the shower-bath would supply. Dogs and other animals apparently quite dead have been recovered by dashing cold water upon them. Another antidote is ammonia (spirits of hartshorn), held near the nostrils.

657. The other cyanides are usually prepared from potassic or hydric cyanide by the replacement of the potassium or hydrogen by other basic radicles. The formation of argentic cyanide has been already given. The presence of a cyanide may be detected by the following tests, which may be applied to a dilute solution of potassic cyanide :

(1.) The peculiar odour of hydric cyanide will be noticed when a few drops of hydric sulphate are added to a portion of the solution in a test-tube.

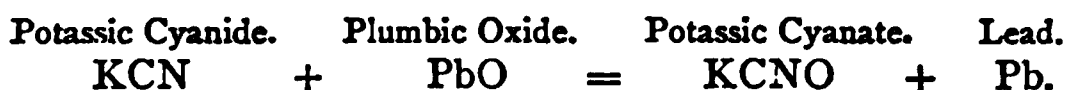
(2.) Solution of argentic nitrate produces a white precipitate, when added in sufficient quantity, the argentic cyanide being soluble in excess of potassic cyanide. The white precipitate is distinguished from argentic chloride, which it resembles, by its solubility in boiling hydric nitrate. A still better method is to wash and dry the precipitate, and then heat it in a small test-tube, and observe whether cyanogen is evolved (see par. 653).

(3.) To a portion of the solution in another tube is added some solution of ferrous sulphate (green vitriol), and then solution of potassic hydrate (caustic potass). A dark precipitate will be formed, and if the liquid, after being slightly warmed, is mixed with some dilute hydric chloride, a deep-blue ferric ferrocyanide (Prussian blue) will remain.

(4.) If a little of the solution is evaporated to dryness with a

few drops of yellow ammoniac sulphide, a little water poured on the residue, and then a drop of ferric chloride added, a deep blood-red solution will be formed. This, which is a most delicate test, depends on the formation of a sulphocyanide, a radicle containing sulphur as well as carbon and nitrogen. The composition of this radicle, and also of the ferrocyanides and ferricyanides, will be referred to under the head of IRON.

(5.) Many of the cyanides have a great tendency to combine with oxygen, each molecule of a cyanide taking up one atom of oxygen, and forming a salt called a cyanate. In illustration of this, about 2 grms. of potassic cyanide may be melted in an iron or porcelain (not platinum) cup, and about the same weight of plumbic oxide (litharge) added gradually. A globule of metallic lead will be found at the bottom of the cup when the mass is cool.



For this reason, potassic cyanide is much used in analysis as a reducing agent.

Section V.—Monatomic Elements.

658. We have now examined the properties of four elements—hydrogen, oxygen, nitrogen, carbon—one belonging to each of the four principal classes into which elements are divided, on account of the difference in their saturating power or capacity of replacing one another in combination. A short explanation of this ‘atomicity’ is given in Chap. XIV. section ii., and in future the elements will be described in the order suggested by their generally received atomicities. We proceed, then, to examine a very well defined group of monatomic elements, consisting of chlorine, bromine, iodine, and fluorine. These elements are connected by the closest chemical analogies, which will be best understood by a recapitulation at the end of the section. In the meanwhile it is sufficient to observe, that one atom of each forms with one atom of hydrogen a compound possessing strong acid properties.

CHLORINE.

| | Symbol. | Weight. | |
|---------------|-----------------|---------|----------------------------|
| Atom..... | Cl | 35.5 | 1 litre weighs 3.173 grms. |
| Molecule..... | Cl ₂ | 71 | Density = 2.453. |

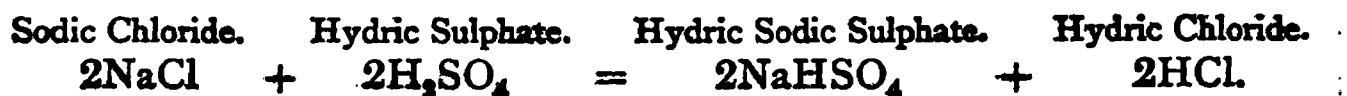
659. *Distribution.*—Chlorine exists abundantly in nature, chiefly in combination with sodium, in sea-salt and rock-salt. It occurs in the majority of soils and natural waters; and is found constantly present in plants and in animals. Its name is derived from the Greek *χλωρος* (chloros), yellowish green, in allusion to the peculiar colour of the gas. It was discovered by the Swedish chemist Scheele in 1774.

660. *Preparation.*—Chlorine is usually prepared from common salt (sodic chloride). When this substance is acted upon by hydric sulphate, we obtain, not chlorine, but the compound of chlorine and hydrogen, hydric chloride. If, however, an oxidising substance is present, the oxygen yielded by it combines with the hydrogen, and chlorine alone is evolved as gas. The usual oxidising agent employed is manganic oxide, which has already been noticed as a source of oxygen. Thirty grammes of powdered sodic chloride should be mixed with an equal weight of manganic oxide, and placed in a flask fitted with a funnel and delivery tube, like that used for preparing hydrogen. Sixty cubic centimetres of strong hydric sulphate should be diluted with an equal volume of water, and when cool, poured into the flask. When a gentle heat is applied, the gas comes off rapidly, and may be collected over the pneumatic trough filled with warm water, since chlorine is less soluble in warm water than in cold water. If a good draught cupboard can be used, the gas, from its great weight, may be easily collected by displacement, like carbonic dioxide. In consequence of the irritating and suffocating action of chlorine on the lungs, as little of it as possible should be allowed to escape into the room where it is prepared. The jars should be filled with water before the collection of the gas is commenced; and the latter

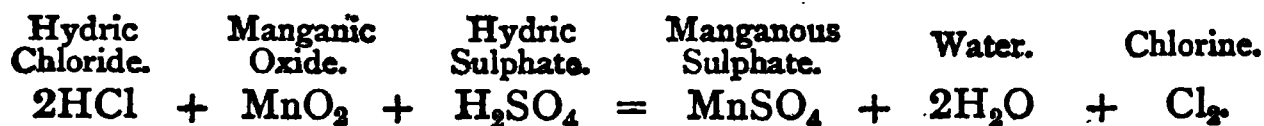
should be received in jars from the first, without allowing the air in the retort to pass into the apartment.*

661. The reaction may be considered to consist of two stages.

(1.) The formation of hydric chloride—thus:



(2.) The decomposition of the hydric chloride by oxygen evolved from the manganic oxide by the action of hydric sulphate—thus:



Another good process for making chlorine, which is often employed on the large scale in chemical works, is to heat manganic oxide with moderately strong hydric chloride. In this case only one-half of the chlorine in the hydric chloride is evolved as gas, the rest remaining in combination with manganese.†



662. *Properties.*—No gas has more marked properties than chlorine, or admits of a greater number of interesting experiments being performed with it. We shall mention these properties in connection with the experiments which may be tried in illustration of them.

(1.) Chlorine, as its name implies, has a yellowish-green colour, a colour markedly visible by daylight, especially if a large jar of the gas be placed side by side with one of air in front of a white object, such as a sheet of paper. The peculiar tint of the gas is less distinguishable by artificial light.

* To get rid of any surplus gas, some solution of common washing-soda may be poured into the bottles and shaken up to absorb the chlorine.

† A process has lately been patented by Mr Weldon for recovering the manganese from this combination in a form in which it can be again used for the manufacture of chlorine. Excess of slaked lime is added to the solution of manganous chloride, and air is then blown through the mixture. The manganous hydrate at first formed, readily absorbs oxygen from the air, becoming manganic hydrate, which can be again used to decompose hydric chloride.

(2.) The odour of chlorine is peculiar. When in small quantity, it is not unpleasant, and resembles that of fresh sea-weeds, or what has been called, characteristically enough, the smell of the sea. In larger quantity, the gas excites severe coughing, oppression of the chest, and sometimes even spitting of blood. If breathed undiluted, it produces immediate suffocation. The student, accordingly, must be careful, in uncovering jars of the gas, not to hold the mouth or nostrils directly over them; and experiments are best tried in a room with the windows open, or, still better, in one with a fire producing a considerable draught, so that the experimenter can hold the jars between himself and the fire, and thereby secure that the gas which escapes shall pass away by the chimney. With all precautions, more chlorine than is agreeable will enter the lungs of the unpractised experimenter. It is well, therefore, to know that its irritating effects are considerably lessened by inspiring a moderate quantity of the vapour of sulphuric ether or alcohol.

(3.) The density of chlorine, which is nearly two and a half times as heavy as air, has been already alluded to. Its weight may likewise be illustrated by pouring it from one vessel to another, when its course may be marked by its colour, or by its characteristic action on chemical compounds, such as argentic nitrate in solution, with which chlorine, like hydric chloride, produces a white precipitate.

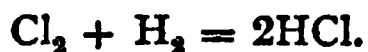
(4.) Chlorine becomes a liquid, at ordinary temperatures, under a pressure of about 4 atmospheres; but it has never yet been solidified. Faraday obtained liquid chlorine by gently heating the chlorine hydrate mentioned below in a strong glass tube, bent near its middle to an obtuse angle, and hermetically sealed. The substance is decomposed into water and liquid chlorine, which latter can be distilled over into the other branch of the tube. The experiment is a dangerous one, since the tubes sooner or later explode, owing to the action of chlorine upon water, oxygen, an uncondensable gas, being evolved.

(5.) Water at 15° dissolves twice its volume of the gas, and

acquires its odour, taste, colour, and other properties. This solution may be prepared by following the method recommended for procuring that of sulphurous anhydride and hydric sulphide. This solubility of chlorine makes it advisable to add some boiling water to the contents of the pneumatic trough, so as to raise it to the temperature of about 35° before collecting the gas. Chlorine-water, which is a useful reagent, must be kept in the dark. If exposed to direct sunlight, the chlorine combines with the hydrogen of the water, and its oxygen is liberated. When a strong solution of chlorine is cooled to 0° , yellow crystals are formed, consisting of a definite chlorine hydrate, represented by the formula, $\text{Cl}, 5\text{H}_2\text{O}$.

(6.) The affinity of chlorine for metals may be illustrated by taking antimony reduced to powder, and shaking it into a jar of the gas. The antimony takes fire, and burns brilliantly, combining with the chlorine to form antimonious chloride (SbCl_3). In like manner copper and gold-leaf introduced into the gas become red-hot, and are converted into their respective chlorides.

(7.) The characteristic affinity of chlorine for hydrogen may be shewn by mixing the gases in equal volumes. They will not unite in complete darkness; but they combine, with explosion, if exposed to the direct sunbeam, and more slowly in diffuse daylight. It is more convenient, when experimenting, to determine their union by passing an electric spark through the mixture, or applying a light to it. The explosion is more feeble than with oxygen and hydrogen, and the light is faint. The product of combustion is hydric chloride, which will redden infusion of litmus poured into the jar after the explosion.



If sunlight is not available, the light obtained by burning a piece of magnesium wire close to the jar containing the mixed gases (which should be lightly closed by a cork), will generally determine the combination. The more accurately the gases,

are mixed in equal volumes, the more sensitive the mixture is to light.

(8.) Chlorine supports but feebly the combustion of such combustibles as burn most brilliantly in air, owing to its slight affinity for carbon. If a lighted candle, accordingly, be plunged into the gas, it burns with a smoky flame; the chlorine uniting only with its hydrogen, forming hydric chloride, and rejecting its carbon, which shews itself as soot.

663. The intense affinity of chlorine for hydrogen, and its corresponding indifference to carbon, are still more strikingly illustrated by dipping a piece of thin paper soaked in pure spirits of turpentine, a compound of carbon and hydrogen, into the gas. The turpentine bursts into flame, hydric chloride is produced, and the jar becomes covered internally with a deposit of carbon.

(9.) Chlorine unites with olefiant gas, as has been mentioned under that substance. It combines also with carbonic oxide, as may be shewn by mixing the gases in equal measures, and exposing the mixture to sunshine. They rapidly but silently unite, contracting to half their volume. The compound they produce is called carbonyl chloride, $(CO)''Cl_2$, and likewise *phosgene* (more properly, *photogene*)—that is, light-produced gas. Its production illustrates very strikingly the curious power of sunlight in accelerating chemical combination.

(10.) The most important of all the properties of chlorine is that of bleaching, by which term is implied a power to destroy vegetable and animal colours, but not necessarily those of mineral compounds. The destruction of colour is complete and final.

664. Chlorine bleaches only when associated with water. If deprived of moisture, as it may be by transmitting it through bottles containing oil of vitriol, or tubes filled with fragments of calcic chloride, it will not destroy the tint of a dry colouring matter, provided, at least, sunlight be excluded. In proof of this, a piece of paper stained with infusion of litmus, and thoroughly dried, may be placed at the bottom of a dry glass

bottle, which is then to be filled with dried chlorine by displacement. If the bottle be now closed with a stopper, and set aside, the paper will be found to resist the bleaching power of chlorine for days or weeks, even though moisture be not altogether absent. But if a few drops of water are added, the colour will give way in a few minutes.

665. Other experiments may be made in illustration of the bleaching action of chlorine. The gas or its solution may be poured into vessels containing infusion of litmus, of purple cabbage, of turmeric, of violets, or indeed of any coloured vegetable substance. Ink likewise may be taken, and infusion of cochineal or carmine, to represent an animal colouring matter. The tints of all these bodies will be rapidly and totally destroyed by chlorine. Printing-ink, however, which is composed of lampblack, is not affected by chlorine, as may be shewn by placing a page of a book or other printed matter in a bottle of chlorine.

666. When bleaching is practised on the large scale, a compound formed by the action of chlorine on quicklime, called 'chloride of lime,' or 'bleaching-powder,' is preferred to chlorine. Experiments with this substance will be given under the head of HYPOCHLORITES.

667. A property of chlorine not less important than that of bleaching, is the power it possesses of destroying animal effluvia and offensive odours. It is of great service, accordingly, as a disinfectant in fumigating apartments in which noxious animal matters have collected, or persons have resided whilst suffering from infectious diseases. It admits of valuable application also for the purification of the air of sick-chambers whilst occupied by invalids. The chlorine is evolved in the latter circumstances by adding 'chloride of lime' to hot water mixed with a few drops of almost any acid. Chlorine may in this way be set free in sufficient quantity to destroy unpleasant effluvia, without occasioning annoyance to the patient. Where apartments to be fumigated are not inhabited, the chlorine may be evolved from hydric chloride and manganic oxide in the way already described.

668. The compounds formed by chlorine with other radicles are called CHLORIDES, of which the best example is common salt, sodic chloride. The more important of these will be described under the respective metals. The best test for the presence of chlorine, whether free or combined, is a soluble salt of silver, argentic nitrate being generally taken. When a solution of this salt is added to any solution containing chlorine or a chloride, a white curdy precipitate of argentic chloride is formed, which is insoluble in boiling hydric nitrate, but is readily dissolved by ammonia. All chlorides, moreover, evolve chlorine gas when heated with manganic oxide and hydric sulphate.

HYDRIC CHLORIDE.

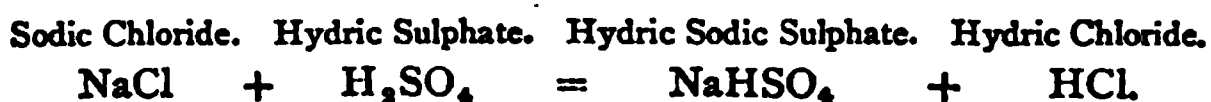
| | Formula. | Weight. | |
|---------------|----------|---------|--|
| Molecule..... | HCl | 36.5 | 1 litre weighs 1.631 gm. Density = 1.261. |

COMPOSITION.

1 litre yields :

$\frac{1}{2}$ a litre of chlorine, weighing 1.586 gm.
 $\frac{1}{2}$ a litre of hydrogen, " 0.0448 "

669. *Preparation.*—Hydric chloride is formed, as already mentioned, by the direct union of hydrogen and chlorine. It is usually prepared by heating sodic chloride with strong hydric sulphate. The sodic chloride should be previously fused in a crucible or iron ladle (a bright red heat being required), in order to lessen the surface exposed to the acid, otherwise the action is not under control. About 30 grms. of the fused salt in lumps may be placed in a retort or flask, fitted with funnel and delivery tube, and 60 c.c. of strong hydric sulphate poured on. No heat at first, and afterwards only a gentle heat, is required. The gas must be collected either over the mercury trough or by downward displacement. The reaction is a simple one, the sodium of the salt and some of the hydrogen of the acid changing places, thus :



A small quantity of the gas may be conveniently obtained for experiments by boiling about 30 c.c. of the strongest commercial 'muriatic acid,' which is a solution of hydric chloride, in a flask. The gas is given off, not absolutely anhydrous, but sufficiently free from moisture to permit its characteristic properties to be examined. The bottle may be known to be filled, by acid fumes issuing freely from its mouth, when the tube is to be withdrawn, and the mouth of the bottle closed with the thumb.

670. It is a colourless, invisible gas, forming dense white fumes when it meets moist air, and possessing a pungent, irritating odour. It has a strong, sour taste, and a powerful action on vegetable colours. Water dissolves nearly 480 times its volume of it, so that it cannot be collected over the water pneumatic trough. Jars may be filled with it over mercury; but as it is heavier than air in the proportion of 1.247 to 1.000, it may be made to displace air, and so to fill dry vessels. The following experiments may be tried with it:

(1.) If a bottle, closed with a glass plate, or the thumb, not a stopper, is opened below water coloured blue with litmus, the liquid will rush up with great force, and at the same time become red, so that by the one experiment the great solubility of the gas in water, and its possession of acid properties, may be illustrated.

(2.) If a candle be plunged into a jar of the gas, it is extinguished without setting fire to the hydric chloride, which is neither combustible nor a supporter of combustion.

671. When hydric chloride is added to a metallic oxide, it forms a salt with it belonging to the class of chlorides. Thus, when sodic hydrate is employed, sodic chloride is formed, together with water:



When, instead of the oxide, the metal itself is taken, the hydrogen of the acid, if any action takes place, is evolved as gas. Thus, with zinc,



The properties of the chlorides have been already given under **CHLORINE**.

672. When hydric chloride is caused to act upon ammonia, yet another kind of action appears to take place, the two gases uniting directly, to form a single salt, ammonic chloride (sal-ammoniac):



The reaction will be further considered under **AMMONIUM**; in the meanwhile the experiment is a striking one, and may be described here. Two wide-mouthed bottles, the one filled with hydric chloride, the other with ammonia, are taken, and their stoppers replaced by glass plates.* The mouth of the bottle containing ammonia should then be brought just above the mouth of the other bottle, and the glass plates removed. The position of the bottles may then be reversed, in order that the heavier gas, the hydric chloride, may fall through the lighter gas, the ammonia. Dense white fumes are at once formed, the two invisible gases combining to form a white solid, while much heat is evolved.

673. The ordinary 'muriatic acid' of the shops is a strong solution of hydric chloride in water, formed by passing the gas through a series of bottles half filled with water. The tube conveying the gas dips below the surface of the water in the first bottle, and the gas as it bubbles through is rapidly absorbed, the water becoming hot, and increasing in bulk. Any gas which escapes is conveyed by a similar tube to the second bottle, and so on. The saturated solution of hydric chloride is a colourless, fuming liquid, containing about 42 per cent. by weight of the acid, its specific gravity being 1.2.† It is of great use in the laboratory as a reagent, and large quantities are employed in the arts in the preparation of chlorine and sal-ammoniac, and in dye-works.

* The mouth of the bottle of ammonia should be held downwards while this is being done, on account of the lightness of the gas.

† It is often yellow, owing to the presence of iron, and arsenic is sometimes present as an impurity. It should be obtained pure for laboratory use.

674. A mixture of 3 measures of strong hydric chloride (solution) and 1 measure of hydric nitrate forms a liquid which has the property of dissolving gold, and was hence called by the alchemists, *Aqua regia*, gold being considered by them the king (*rex*) of metals. The real solvent in this case is chlorine in the 'nascent' state, the reaction being expressed in the following equation:



675. The composition of hydric chloride may be ascertained in several ways.

(1.) It has been already mentioned that it is formed by the direct union of equal volumes of hydrogen and chlorine. The weights of these equal volumes are as 1 : 35.5.

(2.) When a concentrated solution of the gas is electrolysed, we find eventually equal volumes of hydrogen and chlorine given off from the negative and positive poles respectively.

(3.) When a known volume of the gas is heated with sodium, or shaken up with an amalgam of sodium and mercury, one-half of it disappears, sodic chloride being formed, while the remaining half may be proved to be hydrogen. The sodic chloride contains no hydrogen (like the compound formed when the metal acts upon water, page 148), but may be caused to yield half a volume of chlorine.

(4.) We have never been able to take out either the hydrogen or the chlorine from hydric chloride in several portions, and we are led to believe that the molecule of the substance contains 1 atom of hydrogen associated with 1 atom of chlorine, the weights of these atoms being as 1 : 35.5. This result, it will be observed, indicates also the atomic weight of chlorine.

COMPOUNDS OF CHLORINE WITH OXYGEN AND HYDROGEN.

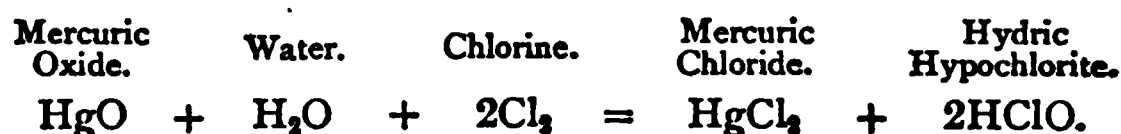
676. There are five known oxides of chlorine, all forming acids when combined with water. Their names and composition are as follows:

| | | |
|-----------------------------|-------------------------|------|
| Hypochlorous Anhydride..... | Cl_2O | 87 |
| Chlorous Anhydride..... | Cl_2O_3 | 119 |
| Chloric Peroxide..... | Cl_2O_4 | 135 |
| (Chloric Anhydride.....) | Cl_2O_5 | 151) |
| (Perchloric Anhydride.....) | Cl_2O_7 | 167) |

The last two have not yet been isolated ; the evidence of their existence is that we know compounds, called hydric chlorate (HClO_3) and hydric perchlorate (HClO_4), which, from their analogies, we may expect to yield these oxides. The resemblance between the above series and that of the nitrogen oxides is obvious. There is one missing compound, however, in the chlorine series, the dioxide, Cl_2O_2 , and there is one chlorine oxide—namely, the last, Cl_2O_7 —which has no representatives in the nitrogen series. Further research may supply these gaps.

677. All the chlorine oxides are very unstable, explosive substances, and are seldom prepared. We shall not, accordingly, describe them with the same minuteness as the nitrogen oxides, but dwell chiefly on some compounds which may be derived from them.

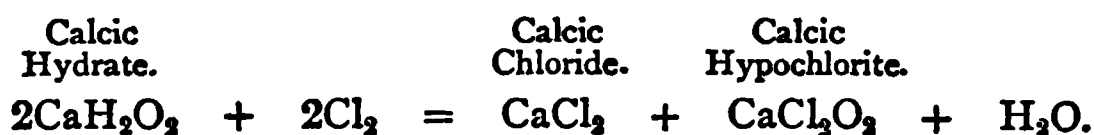
678. *Hypochlorous Anhydride*, Cl_2O .—This substance may be prepared by passing dry chlorine over powdered mercuric oxide, placed in a tube and kept cool. The chlorine combines with the mercury to form mercuric chloride, while another portion combines with the oxygen to form hypochlorous anhydride. The latter is a yellow gas, which, when slightly heated, decomposes with explosion into chlorine and oxygen. It combines with water to form hydric hypochlorite. If, instead of excluding moisture, we place the mercuric oxide in a bottle containing chlorine gas and a little water, and shake the mixture briskly, hydric hypochlorite is formed at once.



The mercuric chloride forms an insoluble compound with the excess of oxide, and may be separated by filtration. The

filtered solution of hydric hypochlorite has a faint sweetish smell, quite distinct from that of chlorine, and exhibits powerful bleaching properties.

679. When chlorine is passed through a solution of potassic hydrate (kept cool) a similar change takes place, potassic chloride and hypochlorite being formed. The solution is used for disinfecting and bleaching purposes, but not to the same extent as the corresponding calcic compound, which is formed when chlorine is passed over slaked lime spread on trays.

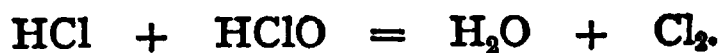


This substance, called chloride of lime, or bleaching-powder, can be readily procured, and is very cheap, so that the student may imitate, by means of it, the process of bleaching cotton. The bleaching-powder is to be mixed with water, and the solution filtered. The liquid bleaches very slightly, so that it may be mixed with the solution of any animal or vegetable colouring matter, and the latter will not be destroyed; but if a drop of any of the stronger acids be afterwards added, the colour instantly disappears, owing to the acid combining with the lime, and liberating the chlorine from its state of inactive combination. Cotton is bleached by soaking it first in solution of bleaching-powder, and then transferring it to a vessel containing very dilute hydric sulphate. In imitation of this process, a piece of turkey-red cotton cloth—that is, calico dyed with madder—may be made colourless in a few minutes by soaking it alternately in a saturated solution of bleaching-powder and in the diluted acid. Stains from port wine, fruit juice, ink, &c. may be readily removed in this way from linen or cotton. The solution of chloride of lime employed for this purpose should be very dilute, and a few drops of vinegar, rather than hydric sulphate, should be added to it after the stained tissue is immersed in the liquid. If bleaching does not speedily occur, a little more chloride of lime and acid may be added; but it is safer to err on the side of too little than too much. The former

fault only protracts the bleaching, and is quite remediable; but if the opposite error be committed, as is too generally the case in domestic bleaching, the excess of chlorine, lime, and acid, which are all powerfully corrosive, totally destroys the fabric.

680. A pretty experiment may be tried with chloride of lime, in imitation of one of the processes employed in calico-printing. A piece of cloth of any colour, provided it owes its tint to an organic colouring matter, such as turkey-red cotton, is made use of. On this cloth, devices are stamped; or, where stamps cannot be procured, are painted with a paste consisting of ordinary flour paste, or gum, to which a little solution of hydric tartrate (tartaric acid) has been added. The cloth is then dried, and afterwards immersed in a hot solution of chloride of lime. The result of this immersion is to develop the devices *in white* upon a coloured ground, in consequence of the acid of the paste with which they were executed decomposing the chloride of lime, and liberating its chlorine, which destroys the colour of the cloth at all the points impregnated with acid, but does not sensibly affect its tint elsewhere.

681. Owing to this decomposition by acids, bleaching-powder is an extremely convenient source of chlorine, and is much used as a disinfectant, and for other purposes where chlorine is employed. The nature of the decomposition, and, indeed, the nature of the substance itself, is not clearly made out. It has usually been regarded as a mixture of calcic chloride and hypochlorite, which yield hydric chloride and hypochlorite, when acted on by acids, and these latter decompose each other, thus:



But bleaching-powder has never been proved to contain calcic chloride in a state of mechanical mixture, and its formula is now regarded as CaCl_2O . In any case, when acted upon by an acid, water, chlorine, and a calcium salt are the ultimate products.

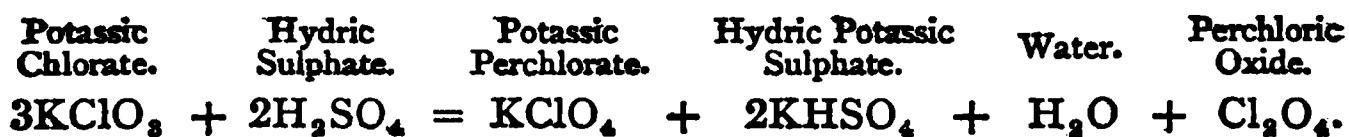
682. Hypochlorites under some circumstances are decomposed in a different way, oxygen being evolved, thus:



This especially takes place when a few drops of a solution of cobaltic nitrate are added to a clear solution of bleaching-powder. Cobaltic oxide is at once precipitated, and determines the evolution of all the oxygen the salt contains; the oxide being itself, probably, alternately reduced and oxidised. This has been employed in practice as a method of preparing oxygen.

683. *Chlorous Anhydride*, Cl_2O_3 .—This substance is obtained by gently heating a mixture of potassic chlorate, arsenious anhydride, and hydric nitrate. It resembles hypochlorous anhydride in appearance and properties. It forms a series of salts, called chlorides, of which hydric chlorite (HClO_2) may be taken as the type.

684. *Perchloric Oxide*, Cl_2O_4 .—This oxide is procured by the action of hydric sulphate on potassic chlorate. Hydric chlorate is probably at first formed, but this decomposes into water, oxygen, and perchloric oxide. Thus:



685. Perchloric oxide is a deep yellow gas possessing a peculiar indescribable odour. It is very soluble in water, to which it communicates its colour. It may be collected over mercury, or by the displacement of air. Its most important property is its explosiveness, which is such, that a very slight elevation in temperature suffices to cause its separation into its elements with great violence.

1st, To observe this, the experimenter may place in a small test-tube about twenty drops of hydric sulphate, and add to it a grain or two of potassic chlorate. The tube should be held in a tube-holder, and its mouth turned away from the experimenter. The materials may be heated by a long paper match, when a deep-yellow gas will fill the tube. If the latter be then

warmed along its length, the gas will detonate sharply and become colourless.

2d, Perchloric oxide supports combustion readily. A very beautiful experiment, which is quite free from danger, may be tried in illustration of this: Six or seven thin chips of phosphorus are placed at the bottom of a champagne or narrow ale-glass along with some crystals of potassic chlorate, and the glass is filled nearly to the top with water. Hydric sulphate is then added by means of a small tube-funnel, such as is fitted to a flask in the apparatus for preparing hydrogen (fig. 40). The long neck of the funnel is made to rest on the bottom of the glass, so that the hydric sulphate may not suffer dilution before it comes in contact with the crystals of potassic chlorate. The heat evolved melts the phosphorus, which takes fire in the presence of the perchloric oxide evolved simultaneously, and burns with great brilliancy. It is advisable to place the glass on a plate, and to cover it with a bell-jar, lest any of the phosphorus should be spirted over the sides of the vessel.

686. *Hydric Chlorate*, HClO_3 , is not itself a substance of particular interest. Its salts, however, are important, and especially potassic chlorate. This substance, which, as well as nitre, is largely consumed in the preparation of lucifer-matches, is prepared by sending a current of chlorine through a solution of caustic potash, and then heating the liquid to boiling. In this reaction there are two stages: 1st, Potassic hypochlorite is formed, as mentioned in par. 679; 2d, This salt is decomposed into a chloride and chlorate.



687. In illustration of this process, the student may send a current of chlorine through a solution of caustic potash till it ceases to turn reddened litmus-paper blue. If the liquid be then gently concentrated by evaporation, it will, on cooling, deposit crystals which are potassic chlorate. On further concentration it will deposit a second set of crystals. These are the more soluble potassic chloride.

688. The process described is very tedious, and requires a large amount of chlorine. The student may content himself with observing, that when a few drops of a strong solution of potass are added to a bottle filled with chlorine, and the vessel shaken, the yellow colour of the gas disappears in a few seconds, owing to its combination with the elements of the alkali.

689. The chlorates are of great importance as sources of oxygen gas, and are, indeed, most powerful oxidising agents. It has been already observed (par. 436, page 167) that they are decomposed by heat into oxygen and potassic chloride. The formation of a chloride may be proved by dissolving some of the residue left in the tube in water, and testing the liquid with argentic nitrate. A white precipitate of argentic chloride will be formed, while potassic chlorate, when pure, gives no precipitate when tested in the same way. If a crystal of potassic chlorate is powdered, and then mixed cautiously with about the same quantity of pounded white sugar on a plate, the addition of a few drops of strong hydric sulphate will cause the mixture to burst into flame.

690. Chlorates may be recognised by the addition of a little strong hydric sulphate to a portion of the suspected substance. If it is a chlorate, the liquid will turn yellow, and the odour of perchloric oxide will be perceived. They are comparatively stable substances, and do not bleach until a reducing agent, such as a solution of hydric sulphite (sulphurous acid), has been added, so as to liberate lower and less stable chlorine oxides.

691. *Hydric Perchlorate*, HClO_4 .—This, the hydrogen salt corresponding to the highest chlorine oxide, Cl_2O_7 , is obtained by the action of strong hydric sulphate upon potassic perchlorate, a salt produced during the decomposition of potassic chlorate by heat, or by acids (preferably hydric nitrate). This salt is comparatively insoluble in water, and may be separated by crystallisation. Hydric perchlorate has been examined with great care by Professor Roscoe (*Chem. Soc. Journal*, xvi. 82). It is, when pure, a dangerous substance, exploding instantly when brought in contact with wood, or any organic substance,

and undergoing spontaneous decomposition at ordinary temperatures.

692. Chlorine forms a remarkable compound with nitrogen, the formula of which is believed to be Cl_3N , analogous to ammonia, H_3N , the chlorine replacing hydrogen, atom for atom. It is perhaps the most formidable of explosive compounds, and requires to be prepared with the greatest caution. To procure it, 20 grms. of pure ammoniac chloride are dissolved in 300 c.c. of distilled water. The solution is placed in a large porcelain basin, having a small leaden saucer lying at the bottom, whilst a litre bottle, full of chlorine, is suspended with its mouth downwards below the surface of the liquid, and directly over the leaden saucer. The liquid rapidly rises within the bottle as it absorbs the chlorine, and drops of a yellow, oily liquid, which is the chloride of nitrogen, collect first on the surface of the liquid, and afterwards sink through the water into the leaden saucer. The bottle must on no account be touched or disturbed whilst the production of the chloride is going on. At the termination of the process, the leaden saucer is cautiously withdrawn, and the chloride may be safely exploded by touching it with a stick dipped in oil. It is immediately resolved into chlorine and nitrogen, with the evolution of heat and light, and the production of a loud noise. It produces a pit, or indentation, on the leaden saucer. Glass, or even cast-iron, would be shattered to pieces. It is exploded by contact with almost every organic substance containing hydrogen, but especially with oleaginous bodies. The greatest care, accordingly, must be taken to secure the freedom of the vessels used in its preparation from grease or impurity of any kind.

693. In addition to the compounds described, chlorine enters into combination with all the other elementary bodies. These combinations will be most appropriately described under the head of the respective elements.

BROMINE.

| | Symbol. | Weight. | |
|---------------|-----------------|---------|---------------------------|
| Atom..... | Br | 80 | 1 litre weighs 6.99 grms. |
| Molecule..... | Br ₂ | 160 | Density of vapour = 5.41. |
| | | | " liquid = 2.98. |

694. Bromine receives its name from the Greek *Βρωμος* (Bromos), a disagreeable smell, in allusion to its powerful and offensive odour. It very closely resembles chlorine and iodine in character, and is intermediate in properties between them—excelling iodine in chemical activity, but being inferior to chlorine. It is a comparatively rare and costly substance, so that it cannot be freely used in experiments.

695. *Distribution*.—It occurs in the same circumstances as iodine—namely, in mineral waters, in the sea, and in sea plants and animals. It is found in these, in combination chiefly with the metal magnesium, as magnesian bromide, MgBr_2 .

696. *Preparation*.—On the continent it is prepared from certain mineral waters rich in it—for instance, that from the Kreuznach spring. In this country it is procured from concentrated sea-water. When the latter is boiled down, with a view to procure from it table-salt, the evaporation is never pushed to dryness. Successive quantities of sea-water are concentrated to a small bulk, the crystals of common salt which separate being removed by means of shovels or colanders pierced with holes. At intervals the residual or mother-liquor is drawn off and set aside. It is a dense oily liquid, containing all the more soluble salts of the sea-water. It is called by the workmen *salt oil*, in allusion to its density, and also *bittern*, in allusion to the unpleasant taste of Epsom salts which it possesses, owing to the large quantity of salts of magnesia which it contains.

697. If the student can procure this bittern, he may prepare bromine from it in the following way: A current of chlorine is sent through the bittern as long as it causes it to darken in colour. The bittern finally acquires the appearance of table-beer. The change in colour is owing to the liberation of

bromine from the magnesian bromide present in the liquid. The chlorine combines with the magnesium, and the bromine separating, dissolves in the liquid, and colours it.



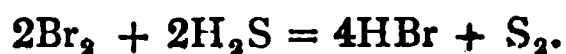
When the liquid is shaken up with ether, the bromine dissolves in the ether, which forms a distinct stratum on the surface. The rest of the liquor, now free from bromine, is drawn off from below, and the ethereal solution is shaken up with solution of potassic hydrate, on which bromine acts like chlorine, a mixture of potassic bromide and bromate being formed.



The bromate present is decomposed by heat, and the potassic bromide is distilled in a retort with manganic oxide and hydric sulphate, as in the manufacture of chlorine. The bromine passes over as a dark-red vapour, and condenses in the receiver along with a little water.

698. *Properties.*—Bromine is the only element which is liquid at ordinary temperatures, except quicksilver. It has a dark, brown-red colour, and is opaque when seen by reflected light. When examined by transmitted light, it appears transparent, and the red tint predominates over the brown. Its odour is peculiar, but in small quantity recalls the smell of the sea, like chlorine and iodine. If cooled down to -12.5° , bromine forms a red crystalline solid, somewhat metal-like. At ordinary temperatures it is markedly volatile, so that, to prevent its loss by evaporation, it is preserved in tightly stoppered bottles under the surface of water. It boils at 63° , yielding a ruddy brown vapour, not distinguishable in colour from nitric peroxide, but quite unlike it in odour. It is soluble in water, and more abundantly in alcohol and in ether. When associated with water it bleaches readily. The taste of bromine is harsh and acrid, and it is a powerful poison. It corrodes the skin, staining it yellow, like hydric nitrate. With starch it forms a yellow or pale-orange compound.

699. Bromine has the same strong affinity for the metals and hydrogen which characterises chlorine, and the compounds formed are called BROMIDES. It combines with phosphorus with great violence, and the phosphoric bromide is readily decomposed by water yielding hydric bromide, a colourless fuming gas resembling in many properties hydric chloride. The nature of the reaction will be explained under the head of HYDRIC IODIDE. A solution of hydric bromide may be obtained by passing hydric sulphide through a solution of bromine :



The best known bromide is that of potassium, KBr, a white salt closely resembling the corresponding potassic iodide, and employed to a small extent in medicine and in the arts. Hydric bromide and bromides are readily identified by the fact, that when exposed to chlorine, or heated with hydric sulphate and oxide of manganese, they give off a ruddy-brown vapour having the characteristic odour of bromine ; and also that their solutions give a pale yellow precipitate when tested with argentic nitrate, which is insoluble in hydric nitrate, and soluble with difficulty in ammonia.

700. No bromine oxide has yet been isolated ; but there are indications of the existence of salts called hypobromites, analogous to hypochlorites, and several bromates are known. To procure potassic bromate, bromine is added to the solution of potassic hydrate till it loses alkalinity. On concentrating the liquid, crystals of a bromate first separate, and afterwards crystals of a bromide. The change that occurs is closely analogous to that which happens when chlorine acts upon alkalies. If the student, accordingly, will turn back to par. 687, and substitute the word bromine for chlorine, he will find the reaction fully explained. Baric bromate, when decomposed by hydric sulphate, yields hydric bromate, a substance closely corresponding in properties to hydric chlorate.

IODINE.

| | Symbol. | Weight. | 1 litre of iodine vapour weighs 11.36 grms. |
|---------------|----------------|---------|---|
| Atom..... | I | 127 | Density of vapour = 8.782. |
| Molecule..... | I ₂ | 254 | " solid = 4.947. |

701. *Distribution*.—Iodine occurs chiefly in sea-weeds, where it is found in combination with sodium or potassium. It is found in land and water plants and animals, especially those living in marine districts. It is a constituent also of many mineral waters, but is very rare as a component of the solid crust of the earth.

702. *Preparation*.—Iodine is prepared from kelp, the fused ashes of burnt sea-weeds. Kelp is manufactured on the western shores of Scotland and Ireland by burning dried sea-weeds in shallow pits till the greater part of the vegetable matter is consumed. The heat thus produced occasions the fusion of the salts contained in the sea-weed; and when the whole cools, it becomes a solid mass, somewhat like gray trap-rock. As the first step towards the production of iodine, the kelp is broken into small pieces and digested in water. Not more than half of it dissolves in that liquid, the soluble portion consisting of sodic and potassic chlorides, sodic carbonate, sodic iodide, and some other less important salts. Of these, the one last named is the most soluble, so that when the solution of kelp is concentrated by evaporation, all the other salts crystallise out first, whilst the sodic iodide is retained in solution after the liquid has been reduced to a very small bulk. This mother-liquor (as it is called) is placed in a leaden retort, together with hydric sulphate and manganic oxide, and on the application of heat iodine distils over.

703. In imitation of this process, the student may place in a retort connected with a receiver a solution of potassic iodide, a salt easily procured. Some powdered manganic oxide is then to be added, and afterwards a little hydric sulphate. When the retort is heated, a beautiful violet vapour will appear, and

condense in the neck of the retort and in the receiver in the form of black shining scales. The reaction is precisely similar to that by which chlorine and bromine are obtained.

704. *Properties.*—Iodine is a bluish-black crystalline solid, with a metallic lustre, greatly resembling plumbago or black-lead in appearance. It is a volatile substance, rising in vapour below 0° , fusing at 107° , and boiling at 178° . It then changes into a very beautiful purple or violet coloured gas, which is more than eight times heavier than air, and is the heaviest gaseous body. The word iodine is derived from *ἰώδης* (Iodes), violet-coloured, in relation to the appearance of its vapour.

705. Iodine has a peculiar odour, somewhat like that of chlorine, yet sensibly different. It stains the skin brown, but the mark is not permanent. It dissolves to a small extent in pure water, but largely if the liquid contain a metallic iodide, such as that of potassium. Alcohol dissolves it readily.

706. Iodine is in small doses a valuable medicine, and in large ones a poison. It is readily distinguished from all other bodies by its odour, its violet vapour, and its action on a solution of starch. In illustration of this, the student may try the following experiments:

(1.) There is no difficulty in observing the odour of iodine, which cannot fail to be noticed.

(2.) The colour of its vapour is well seen by throwing a little upon a hot brick; but this must be done in the open air.

(3.) A more economical and convenient method of exhibiting its tint as a gas, is to place about half a gramme of it at the bottom of a large dry flask, and then to apply heat. The iodine rapidly volatilises, filling the vessel with its vapour, the great density of which is rendered apparent by its dark purple colour at the bottom of the vessel, as contrasted with its rose tint above, and by the sluggishness with which the purple cloud changes its place when the vessel is inclined. At the same time the upper part and sides of the flask become completely covered with dark, black, shining crystals of the condensed iodine.

(4.) A solution of starch is to be prepared by mixing a little starch-powder with 1 or 2 c.c. of cold water, and then pouring on it 30 or 40 c.c. of boiling water. When it is quite cold, a little is to be added to water, and then a few drops of an aqueous or alcoholic solution of iodine. A deep-blue solution is immediately produced, consisting of the iodide of starch. If either of the liquids be warm, the blue compound is not produced; or if the liquid be heated after its production, the blue is destroyed.

(5.) The experimenter can certify this by heating some of the blue liquid in a flask. When it has reached the boiling-point the colour will disappear. If the flask be now suddenly cooled by running cold water on the outside, the blue colour will return. Starch is a test of extreme delicacy for iodine, provided the latter be free; but when its quantity is small, a pale purple or rose tint only is produced.

707. The compounds of iodine, which are called IODIDES, very closely resemble those of chlorine, but there are fewer of them. The most interesting one is the compound of hydrogen and iodine, hydric iodide, which will be described next.

HYDRIC IODIDE.

| | Formula. | Weight. | |
|---------------|----------|---------|--|
| Molecule..... | HI | 128 | 1 litre weighs 5.725 grms. Density = 4.426. |

COMPOSITION.

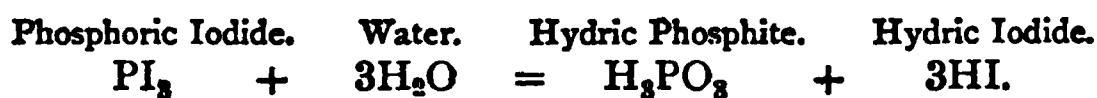
1 litre yields :

$\frac{1}{2}$ a litre of hydrogen, weighing 0.0448 grms.

$\frac{1}{2}$ a litre of iodine gas, " 5.6802 "

708. This gas cannot be prepared in the same simple way in which hydric chloride was prepared. When hydric sulphate is added to potassic iodide, violet vapours of iodine are given off, the hydric iodide and hydric sulphate undergoing partial decomposition into water, iodine, and sulphurous anhydride. It is therefore usually obtained by decomposing phosphoric iodide by water, a reaction alluded to under BROMINE. The

iodine unites with some of the hydrogen of the water to form hydric iodide, while the rest of the hydrogen and all the oxygen form, in combination with the phosphorus, hydric phosphite. Thus :



709. The action of iodine on phosphorus is, as mentioned below (par. 718), rather violent; but the gas may be prepared with perfect safety in the following way: Twenty grammes of iodine are weighed out, powdered, and placed in a small retort flask fitted with a delivery-tube (see fig. 32, page 166). About 3 or 4 c.c. of water are added, and then 1 grm. of 'amorphous' (not ordinary) phosphorus is put in, and the mixture shaken. The reaction begins almost directly, never becoming violent, and, by applying a very gentle heat, the hydric iodide comes over, and may be, from its weight, collected by displacement.

710. In its properties, hydric iodide greatly resembles hydric chloride, but it is much more unstable. When a jar of chlorine is brought near the mouth of a jar of hydric iodide, so that the gases may mix, violet clouds of iodine vapour are formed, the chlorine replacing iodine in combination with hydrogen. The gas cannot be kept for any length of time without a separation of iodine taking place.

711. A solution of the acid is more conveniently prepared by passing a current of hydric sulphide through water in which finely powdered iodine is suspended. The hydrogen of the hydric sulphide combines with the iodine to form hydriodic acid, and the sulphur separates. The liquid is warmed and filtered, and furnishes a colourless solution of hydric iodide, which becomes rapidly brown if exposed to the atmosphere, owing to the combination of the oxygen of the air with the hydrogen of the acid to form water, and the separation of the iodine, which colours the liquid.

712. Hydric iodide is not a substance of great interest; but many of the metallic iodides are important substances. If

hydrogen, which is an explosive substance like the chloride, but not so formidable, and more easily prepared. It is an insoluble black powder, obtained by digesting together iodine and aqueous ammonia, and then collecting the iodide on a paper filter. The iodide explodes spontaneously as it dries. The filter should be cut when moist into several pieces, each of which may be dried separately. A striking experiment may be performed by transferring a small portion of the moist iodide to a thin china plate, and when it is nearly dry, exploding it by the touch of a hot wire. The iodide blows a hole through the plate at the spot on which it lay, without otherwise injuring it.

718. Iodine and phosphorus combine in several proportions. If a fragment of phosphorus, lying on a plate, be sprinkled with iodine, the substances unite, and heat enough is produced to kindle the phosphorus. The experiment is interesting, as supplying an illustration of what is somewhat rare—namely, the combination of two substances presented to each other in the solid state.

FLUORINE.

| | Symbol. | Weight. |
|-----------------|----------------|---------|
| Atom..... | F | 19 |
| (Molecule.....) | F ₂ | 38) ? |

719. *Distribution.*—Fluorine is found in nature pretty widely distributed, but it does not occur anywhere in large quantity. It is never found uncombined, and its most frequent compound is calcic fluoride, more familiarly known as fluorspar, from its occurrence in which this element receives its name. Small quantities of calcic fluoride are found in most fertile soils, and in several natural waters, as well as in the sea. Traces of it, also, are met with in different plants; and it appears nearly constantly to accompany calcic phosphate in the bones of the higher animals, and likewise in shells and corals. It is especially abundant in certain fossil bones. Another source of fluorine is the mineral cryolite, which occurs in Greenland, and is a compound of fluorine, sodium, and aluminium.

720. Fluorine has never been satisfactorily isolated, owing to its great affinity for nearly all substances, and especially for one of the elements of glass (silicon), so that it cannot be prevented from uniting with these, and eluding our observation.

HYDRIC FLUORIDE.

| | Formula. | Weight. | |
|---------------|----------|---------|---|
| Molecule..... | HF | 20 | 1 litre weighs 0.903 grm. Density = 0.698. |

COMPOSITION.

1 litre yields :

$\frac{1}{2}$ a litre of hydrogen, weighing 0.0448 grm.

$\frac{1}{2}$ a litre of fluorine (?), " 0.8582 "

721. Although fluorine itself is so little known, it is otherwise with its compounds, several of which can be easily prepared, and possess striking properties. Of these the most important is hydric fluoride. To procure this substance, fluorspar, a mineral easily procured, is reduced to powder, and heated with hydric sulphate. A change occurs exactly analogous to that which leads to the evolution of hydrochloric acid when hydric sulphate acts on a chloride. The calcium of the fluorspar replaces the hydrogen of the hydric sulphate, forming calcic sulphate; whilst the hydrogen of the acid, uniting with the fluorine of the fluorspar, forms hydric fluoride (HF), which is highly volatile, and passes away in vapour :



722. In the preparation of this acid, glass vessels cannot be employed. A retort of platinum, or of lead, with a receiver of the same metal, must be made use of. Heat is cautiously applied to the retort, and the receiver is kept very cool by surrounding it with ice. The vapour condenses along with a little water into a fuming volatile liquid.

723. Anhydrous hydric fluoride, which has been recently examined with great care by Mr Gore (*Phil. Trans.* 1869, p. 173), is a colourless, very volatile liquid, boiling at 19.5°. It

has an intense affinity for water, and emits dense fumes when in contact with moist air. It is a most dangerous and corrosive substance, and can only be retained in platinum bottles, the stoppers of which are secured by a cement of paraffin. The vapour of the ordinary acid is exceedingly irritating to the lungs, and very corrosive, so that it produces severe sores if allowed to condense on the skin.

724. Its most interesting property, which leads to its employment in the arts, is that of corroding or etching glass, which it does when strong (but not if anhydrous) with great rapidity. Hydric fluoride is employed to act upon glass in two ways. In the one it is intended to etch lines, as of an engraving, or letters, upon a piece of homogeneous glass. In this case the glass is first covered with a layer of beeswax, or engravers' etching-ground (a preparation of asphaltum and turpentine); and the lines or letters are then drawn, or rather, as it were, cut with an etching needle through the covering down to the glass: when the glass is afterwards exposed to the action of the hydrofluoric acid, directed against it in vapour, or poured upon it in the liquid state, it corrodes the glass wherever it is unprotected by the beeswax or asphaltum. In this way tubes, measures, and thermometers may be graduated by the student himself, and the expense of costly pieces of apparatus saved.

725. The other use to which hydric fluoride is put is to produce devices in glass-staining, by a process analogous to that by which white figures are produced on coloured grounds in calico-printing, as described under chloride of lime. The glass to be employed for this purpose consists of two sheets, the one colourless, the other coloured, which have been made to adhere to each other throughout, by heating them in a furnace till they agglutinate, and mutual adhesion takes place.* Let the object of the artist, for example, be to produce a white

* This 'flushed glass,' as it is called, is more generally made by collecting a mass of colourless glass on the end of the iron 'punty' or tube used by glass-workers, and dipping it into a pot of coloured glass. The whole is then blown out together and formed into a sheet in the usual way.

star on a blue ground: a sheet of white glass, plated with one of blue, is taken, and on the latter surface all that is to remain blue is painted over with an asphaltum varnish, whilst the portion which is to appear white (in the case supposed, the star) is left uncovered. A wall of wax is then built round the sheet of glass, and liquid hydric fluoride, somewhat diluted, is poured on, and left till it has eaten away the whole thickness of the blue glass, and brought the white into view. By a similar process, but reversing the portions of the glass left uncovered, the star could be obtained blue on a white ground.

726. It is scarcely worth the beginner's while to distil hydric fluoride, as nothing can be seen, and, moreover, the strong acid is a substance requiring to be handled very cautiously. The power of the acid to etch glass may be sufficiently observed in a simpler way. A small cup, saucer, or porcelain basin, but best of all, a vessel resembling these in shape, made extemporaneously from a piece of sheet-lead (a common lead ink-pot answers well), has some powdered fluorspar placed in it, and hydric sulphate poured upon the spar. A square of glass, large enough to cover the basin, is covered with beeswax, and has a device drawn or written on it with any sharp-pointed body, such as a common pencil, not hard enough to scratch the glass. This is laid with its waxed side downwards, as a cover on the basin, and the latter is gently heated, care being taken that the temperature does not rise so high as to melt the wax. In a few minutes the glass may be removed, and the wax cleaned from it by means of a little hot turpentine, when it will be found deeply and permanently etched.

727. The test for fluorine in combination is the evolution from its compounds, when heated with hydric sulphate, of an acid vapour (hydric fluoride) which etches glass. The student may test for fluorine in this way by heating with hydric sulphate, in a small leaden cup, fragments of a burnt bone reduced to powder, under a cover of waxed glass, with a word or device traced on it. The arrangement must be left in a warm place undisturbed for some hours.

728. Fluorine appears to form no compound with oxygen, being in this respect peculiar among the elements.

729. With silicon, fluorine forms a compound of great interest, the tetrafluoride (SiF_4). To prepare it, a mixture of equal parts of powdered glass and fluorspar is placed in a glass flask with

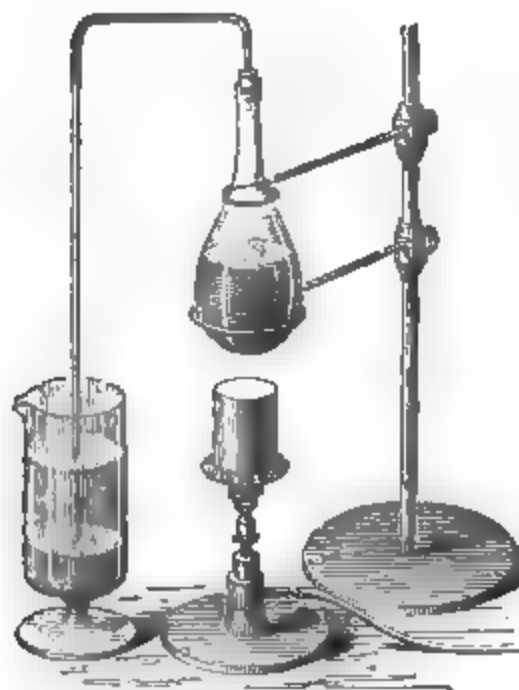
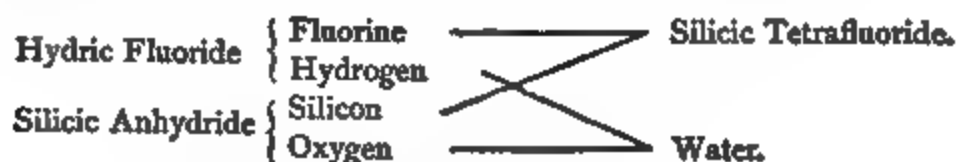


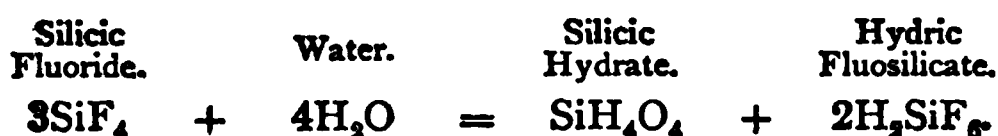
Fig. 71.

twice the weight of strong hydric sulphate. A dry tube twice bent at right angles, fitting the flask by a cork, is conducted to the bottom of a glass jar, and made to dip below the surface of a small stratum of mercury. (See fig. 71.) After the tube has been thus arranged, water is poured over the mercury so as to form a column of some inches in height above it, and heat is then applied to the flask. The hydric sulphate and fluorspar cause the evolution of hydric fluoride, which immediately reacts upon the silicic

anhydride of the powdered glass, so that the hydrogen of the acid combines with the oxygen of the other to form water, and the fluorine of the one with the silicon of the other to form silicic tetrafluoride, which is a colourless, invisible gas, as may be observed in the upper part of the flask and bent tube. It is this body which is the result of the corrosion of glass when hydric fluoride etches it. Thus :



730. When the silicic fluoride meets water, it decomposes it, with formation of silicic hydrate and an acid containing fluorine, silicon, and hydrogen, called hydric fluosilicate (hydro-fluosilicic acid), as shewn in the equation :



This hydric fluosilicate is separated by filtration from the silica, and is valuable as a test for potassium, and for separating it from acids which cannot otherwise be obtained free. Hydric chlorate, for example, as well as hydric perchlorate, bromate, chromate, &c. are obtained by the action of hydric fluosilicate on aqueous solutions of their potassium salts.

731. The silica left on the filter is exceedingly pure, and when dried, presents itself in a state of very fine division. The process, indeed, for fluosilicic acid supplies us with one of the most convenient methods known of obtaining pure silica.

732. The production of silica in this process allows a very pretty phenomenon to be witnessed. Each bubble of silicic fluoride, as soon as it rises out of the mercury into the water, is converted into a little sack or bladder of silica. When these bubbles are broken, the silica exactly resembles in appearance gelatinous starch as it is used in the laundry. If the bubbles of gas succeed each other very slowly, they produce a tube of silica closely resembling one of animal membrane, and extending from the surface of the mercury to the surface of the water. This appearance, however, cannot be produced at will. The object of the mercury is to prevent the silicic fluoride meeting moisture till it has issued from the tube. If the latter dipped directly into the water, it would soon become plugged up by the silica produced, and the gas, unable to escape, might burst the flask, and occasion dangerous accidents.

| | Chlorine. | Bromine. | Iodine. | Fluorine. |
|---|--|--|---|---|
| (A.) Physical. | | | | |
| 1. Condition at 15°..... | Gas. | Liquid. | Solid. | ? |
| 2. Colour of vapour..... | Yellowish green. | Orange. | Violet. | ? |
| 3. Boiling-point of liquid..... | - 60°. | 63°. | 175°. | ? |
| 4. Solubility in water..... | Readily soluble. | Moderately soluble. | Scarcely soluble. | ? |
| (B.) Chemical. | | | | |
| 1. Atomic weight..... | 35.5. | 80. | 127. | 19. |
| 2. Chemical power..... | Displaces bromine, iodine, & fluorine. | Displaces iodine and fluorine. | Displaces fluorine. | |
| 3. Compound with hydrogen— a. Formula..... b. Condition c. Properties..... | HCl. Colourless gas. Heavy; fumes in air; very stable. | HBr. Colourless gas. Heavy; fumes in air; not very stable. | HI. Colourless gas. Heavy; fumes in air; very unstable. | HF. Volatile liquid. Heavy; fumes in air; stable. |
| 4. Usual crystalline form of compounds with metals..... | Cubes. | Cubes. | Cubes. | Cubes. |

ANALOGIES OF THE CHLORINE GROUP.

733. The student cannot fail to have noticed the very close resemblance between the four elements which have just been examined; fluorine, however, standing rather apart from the others. They constitute, in fact, one of the best-defined natural groups with which we are acquainted. Whether this points to the existence of any common constituent in, or even identity of, their atoms, is a question which we are not able to answer. A short recapitulation of the principal points of similarity is given on the opposite page, from which the student is advised to construct for himself a more extended account.

Section VI.—Diatomic Elements.

SULPHUR.

| Symbol. | Weight. | 1 litre of vapour, at 900°, weighs 2.867 grms. Density of vapour = 2.21. " " solid (α) = 2.05, (β) = 1.98, (γ) = 1.95. |
|--------------------------|---------|--|
| Atom.....S | 32 | |
| Molecule..S ₂ | 64 | |

734. *Distribution.*—Sulphur occurs abundantly in an uncombined state chiefly in volcanic districts, where, as on the flanks of Etna and Hecla, it presents itself in large veins, from which it is quarried. It is also extensively diffused through the globe, in combination with the metals, so that the chief ores of silver, lead, zinc, antimony, &c. are sulphides. Much also occurs in combination with iron, forming a well-known mineral, iron pyrites. It is also a constituent of sulphates, which occur frequently. Heavy spar, for example, and gypsum, both abundant minerals, are respectively baric sulphate and calcic sulphate. The sulphates of magnesium, copper, iron, and several other metals, are also found native. It is present in all plants, and is an essential and important ingredient of animals. In the latter, as well as in plants, it exists in a peculiar state of combination, of which a good example is furnished by white of egg, the familiar effect of which in blackening a silver spoon is owing to the sulphur it contains.

735. Sulphur occurs in commerce in two states—*roll* sulphur, which is the substance in a solid state shaped into cylinders by casting it in suitable wooden moulds; and *flowers* (not flour) of sulphur, which present this body in the shape of a fine crystalline powder, procured by condensing its vapour, in imitation of the natural process by which water-vapour changes into snow. Flowers of sulphur are also called sublimed sulphur, and are purer than the substance in rolls.

736. *Properties.*—Sulphur is a lemon-yellow, brittle solid, crystalline in structure, and exhaling a peculiar odour when rubbed. It is a little less than twice as heavy as water, in which it is insoluble, but it dissolves in other liquids, such as oil of turpentine and the fixed oils, but best of all in carbonic disulphide, from its solution in which, it may be procured by evaporation, in large transparent beautiful crystals, of an octahedral form. It is a very bad conductor of heat and electricity. A roll of sulphur held in the warm hand near the ear will be heard to emit a peculiar crackling sound, and if the difference between the temperature of the sulphur and the hand be considerable, will split into pieces. These phenomena are owing to the bad and unequal power of conducting heat which characterises sulphur, in consequence of which, it expands in one direction more than in another when heated, and, as a result, has the more expanded portions separated, and, as it were, torn from the colder and contracted ones.

737. There are at least three allotropic forms of sulphur, distinguished as S_{α} , S_{β} , and S_{γ} , respectively.

(1.) S_{α} . This is the form in which sulphur occurs native, and in which it crystallises from its solution in carbonic disulphide. The crystals are, as above noticed, octahedra with a rhombic base, a form belonging to the right prismatic system, fig. 7. This is the most stable form of sulphur, and all the other forms have a tendency to return to it.

(2.) S_{β} . Pieces of roll sulphur are heated gently in a crucible or cup placed in hot sand. It melts at 115° , and forms a clear, thin, limpid, yellow liquid. It is then allowed to cool slowly,

and when a solid crust has formed on its surface, this is pierced with a heated rod, and the still fluid portion poured out into cold water. It will be found, on breaking the crucible, that the hollow is lined with transparent yellow needle-like crystals, in the form of prisms belonging to the oblique prismatic system, fig. 9, A, page 39. These are totally distinct from, and incompatible with, the octahedral form above mentioned. Moreover, sulphur in this form has a rather lower density than S_{α} . These prisms soon become opaque, and are, in fact, though retaining their apparent shape, converted into aggregations of minute octahedra.

(3.) S_{γ} . The liquid sulphur, which, in the last experiment, was, when near its solidifying point, poured into water, will be found to have congealed into a yellow, crystalline, brittle solid, like the original roll sulphur. But if another portion is heated in a tube or flask, and after it has melted, the heat be still continued, the liquid grows darker in colour, and much thicker in consistence, so that between 170° and 190° it resembles in appearance treacle, and is so viscid and sluggish in its movements, that it is some time before it begins to flow from a vessel containing it, after that has been inverted. If liquid sulphur be poured into water whilst in this treacly condition, it consolidates into a soft, elastic, transparent substance, of a dark-yellow or pale-brown colour, much resembling caoutchouc in some of its properties, and totally unlike ordinary sulphur. It may be preserved in this state for some time, and can be drawn out into long elastic threads like india-rubber, but in a few days it returns to the hard crystalline state, being, in fact, for the most part reconverted into S_{α} . The change may be quickly effected by heating the elastic threads to 100° . This form of sulphur is not soluble in carbonic disulphide, and its density is 1.95.

738. When any of the above varieties of sulphur is heated to about 260° , it becomes more liquid again, though not so fluid as it was at 120° ; and when it reaches 440° , it boils, and gives off a deep yellow vapour, which catches fire in oxygen or air,

but which, if air is excluded, may be distilled and condensed into ordinary sulphur. One great proof of the chemical identity of the different forms of sulphur is, that they are all convertible by heat, without change of absolute weight, into S_8 .

739. The vapour of sulphur, at temperatures near its liquefying point, is 96 times as heavy as the same volume of hydrogen, 1 litre weighing 8.601 grms. According to this, the molecule of sulphur would be 96 times as heavy as the molecule of hydrogen, and, supposing that the molecules were composed of the same number of atoms (par. 380, page 144), the atomic weight of sulphur would be 96. But chemical reasons lead us to conclude that the atomic weight of sulphur is 32, or one-third of the above number; and for a long time this anomaly remained inexplicable. It has, however, been found that at a temperature near 1000° , the vapour of sulphur undergoes a sudden expansion to 3 times its former volume, so that 1 litre weighs 2.867 grms.—that is, 32 times as much as a litre of hydrogen; and thus the discrepancy disappears. This has been already alluded to in par. 402, page 152.

740. Sulphur unites with nearly all other radicles, forming a class of compounds called **SULPHIDES**. Copper, for instance, in the form of fine wire, burns when introduced into sulphur vapour, forming cupric sulphide. Iron also may be made to burn in sulphur vapour just as in oxygen, and forms ferrous sulphide. Most of these sulphides will be described hereafter.

SULPHUROUS ANHYDRIDE.

| | Formula. | Weight. | |
|----------------|----------|---------|--|
| Molecule | SO_2 | 64 | 1 litre weighs 2.860 grms. Density = 2.211. |

COMPOSITION.

1 litre yields :

1 litre of oxygen, weighing 1.430 gm.
 $\frac{1}{2}$ a litre of sulphur vapour, " 1.430 "

741. When sulphur is kindled in the air, it burns with a blue flame, and evolves a highly characteristic odour, distinguished as that of burning brimstone, which is not the smell

of sulphur itself, but that of sulphurous anhydride. If the experiment of burning sulphur in oxygen described under that gas be repeated, the phenomena described above will be witnessed still more fully, and the production of an acid—namely, hydric sulphite—may be demonstrated by pouring infusion of litmus into the jar in which the sulphur has been burned. When oxygen is thus converted into sulphurous anhydride, it undergoes no change in volume, although it doubles its weight; 32 grms. of oxygen combining with as many of sulphur to form 64 of sulphurous anhydride.

742. *Preparation.*—The gas is usually prepared in the laboratory, not in the above direct way, but by the decomposition of hydric sulphate in the following manner: Mercury (about 30 grms.) is heated with an equal weight of strong hydric sulphate in a retort or flask, until effervescence occurs. The change may be represented as consisting of two stages: (1.) The replacement of the hydrogen of the hydric sulphate by mercury, thus:



(2.) The partial deoxidation of another portion of hydric sulphate by the hydrogen—thus:



Or, combining the two equations:



Copper may be used in place of the more expensive mercury, with the same result. The gas, owing to its solubility, cannot be collected over water. The mercurial trough may be used, but the gas can, from its high density, be readily collected by downward displacement (like carbonic dioxide, page 229). It is advisable to interpose a small wash-bottle (as in fig. 57), containing a little water, to retain the fine spray of hydric sulphate which is apt to come over.

743. *Properties.*—Sulphurous anhydride is a colourless invisible gas, with a pungent suffocating odour, recognisable as that of burning sulphur. It is very soluble in water, 1 litre of water

at 15° dissolving 40 litres of the gas, and forming a solution of hydric sulphite,



The following experiments will illustrate the chief properties of the gas :

(1.) A candle plunged into a jar of the gas will at once be extinguished. Sulphurous anhydride, indeed, like carbonic dioxide, exerts a positively prejudicial influence on combustion, and is highly poisonous.

(2.) Its great density (it is more than twice as heavy as air) may be shewn by pouring it downwards upon a lighted taper, as in the case of carbonic dioxide (par. 588, page 228).

(3.) A little infusion of litmus may be poured into a bottle containing it, and the mouth of the bottle closed by the thumb. If the bottle be then briskly shaken for a few minutes, and its mouth afterwards opened whilst under water, the latter will rush up with great violence, and nearly or entirely fill the vessel. In this way both its action on colouring matter and its great solubility in water may be demonstrated by one experiment.

(4.) It bleaches vegetable colours, however, as well as changes their tints, and is employed in the arts to bleach wool, silk, and straw. To demonstrate this property, a flower (such as a red rose) may be hung in a vessel of the gas, or suspended over burning sulphur, when its colour will slowly disappear ; or an infusion of the purple cabbage to which a little potass has been added, so as to change it to green, may have a current of sulphurous anhydride sent through it, when it will be observed first to grow red, and then to become colourless. The colour, however, is not completely destroyed, as it is by chlorine ; for if the bleached cabbage infusion be divided into two portions, and a little hydric sulphate added to the one, and potassic hydrate to the other, a red tint will be developed in the former, and a green in the latter.

(5.) Sulphurous anhydride has a remarkable power of arresting animal decomposition, and preventing putrefaction. In illustration of this, a solution of the gas may be added to a

portion of dissolved glue or isinglass, whilst another portion of the latter is kept unacidulated, for the sake of comparison. The simple solution will be found to putrefy long before the other shews any signs of decomposition.

744. Sulphurous anhydride may be condensed into a liquid without much difficulty, either by cold or pressure (par. 205, page 71). When the gas is passed through a U-shaped tube, placed in a freezing mixture of ice and salt (par. 184), it becomes a colourless liquid, which may be preserved in a strong tube, hermetically sealed before the blow-pipe. It boils at -10° , and sulphurous anhydride would hence be known in the Arctic regions as a very volatile liquid, instead of a gas. It may also be liquefied by a pressure of about 3 additional atmospheres (equivalent to a column of mercury 2.28 metres high) at ordinary temperatures.*

745. *Sulphites*.—When sulphurous anhydride is passed into water in an apparatus such as that described under HYDRIC SULPHIDE, a solution containing an acid, hydric sulphite, is obtained, which may be taken as the type of a series of salts called SULPHITES:



While sulphurous anhydride itself shews no tendency to absorb oxygen, hydric sulphite most readily combines with it, and it is much used in the laboratory and in manufactories as a reducing agent. For instance, if a solution of hydric sulphite is added to the deep blue liquid obtained by mixing a little starch with a solution of iodine (par. 706, page 280), the liquid at once becomes colourless, hydric iodide being formed. In this reaction water is decomposed, its oxygen combining with the hydric sulphite, while its hydrogen is taken up by the iodine.



* The liquefaction may be shewn by means of the apparatus described at page 139, especially if the temperature is slightly lowered by surrounding the upper part of the tube, A, with cotton wool soaked in ether.

Again, when hydric sulphite is warmed with a solution of auric chloride, metallic gold is precipitated.

746. The sulphites may be recognised by these reducing properties, and also by the liberation of sulphurous anhydride on addition of hydric sulphate.

SULPHURIC ANHYDRIDE, OR TRIOXIDE.

| | Formula. | Weight. |
|---------------|-----------------|---------|
| Molecule..... | SO ₃ | 80. |

747. Sulphur, when burned in oxygen, shews no tendency to combine with more than 2 atoms of oxygen. But when the sulphurous anhydride formed is mixed with half its volume of oxygen, and passed through a tube containing heated spongy platinum, the gases combine, and white fumes of sulphuric anhydride are formed:



This substance, which is generally prepared by heating Nordhausen acid (see below), is a soft solid, which may be cut and moulded like wax. It boils at 35°, and when distilled, condenses in tufts of white slender needles, like thistle-down. Its most interesting property is its intense affinity for water. The acid is most conveniently retained in hermetically sealed tubes, and when one of these is broken and a little water poured on the contents, they hiss like red-hot iron when quenched in water, and give off dense corrosive fumes, forming hydric sulphate.



HYDRIC SULPHATE (SULPHURIC ACID).

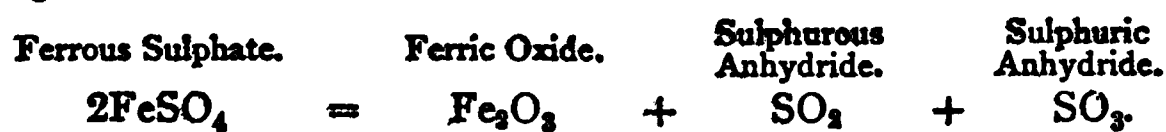
| | Formula. | Weight. | |
|---------------|--------------------------------|---------|----------------------------|
| Molecule..... | H ₂ SO ₄ | 98 | Density of liquid = 1.842. |

748. This may be considered the most important of the acids, both on account of its own properties, and because of

its extensive employment in the manufacture of other valuable reagents, such as hydric nitrate, chloride, and acetate, and also sodic carbonate and sulphate, and many other dyes and chemical products.

749. *Preparation.*—Hydric sulphate is prepared for commercial purposes in two ways: 1st, by heating ferrous sulphate (green vitriol); 2d, by adding oxygen to sulphurous anhydride through the medium of nitric peroxide, in presence of water.

750. The variety of hydric sulphate obtained by the first process goes by the name of Nordhausen acid, from the place in Saxony where it is chiefly prepared. It is also called Saxon or fuming sulphuric acid. The composition of crystallised ferrous sulphate is represented by the formula $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. It is first strongly dried, the effect of which is to expel the greater part of the water it contains. About a seventh part of that, however, is always and purposely retained. The dried ferrous sulphate is then exposed to a red heat in stoneware retorts. A dense oily liquid collects in the receivers, which seems to be a combination of a molecule of ordinary hydric sulphate (H_2SO_4) with a molecule of sulphuric anhydride (SO_3), its formula being $\text{H}_2\text{S}_2\text{O}_7$. The primary decomposition of ferrous sulphate may be expressed thus:



The sulphuric anhydride then unites with the water which is retained in the salt.



751. Nordhausen acid is employed in the arts for dissolving indigo, an acid solution of which is extensively employed in dyeing blue. It is likewise an object of great interest to the chemist, as it enables him to procure sulphuric anhydride. For this purpose, the strongest Nordhausen acid is gently heated in a retort connected with a receiver kept very cold. The additional molecule of sulphuric anhydride is then given off, and ordinary hydric sulphate (H_2SO_4) remains behind.

752. The title oil of vitriol is, in strictness of speech, more applicable to this Nordhausen acid, to which it was originally applied, because that substance is a dense *oily* liquid, obtained by distilling green *vitriol*. The term, however, is now restricted to the weaker English acid, which is prepared in the following way: Sulphur, or iron pyrites, is heated in a furnace, A, fig. 72,

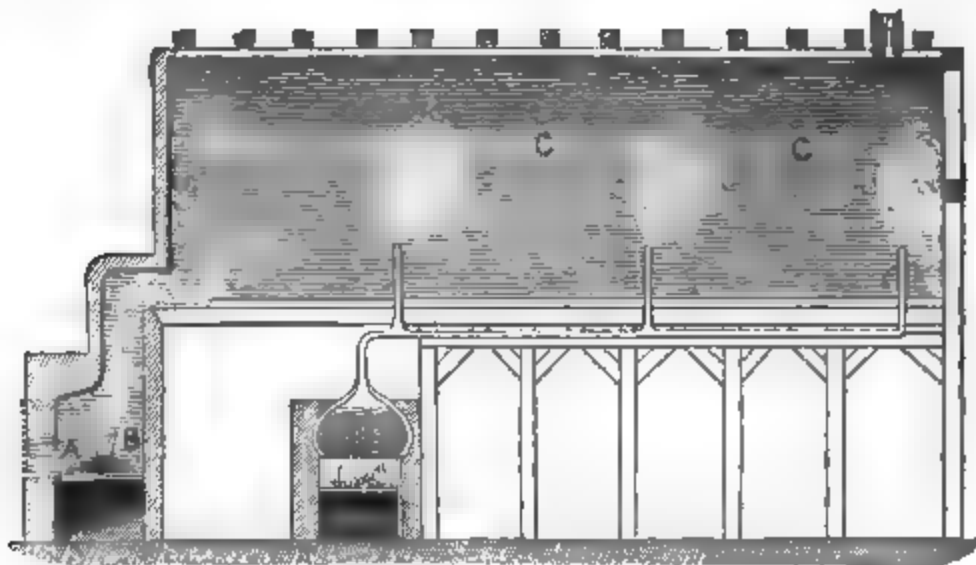
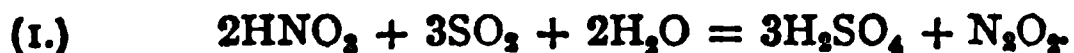


Fig. 72.

and freely supplied with air until it begins to burn. In the upper part of the furnace is suspended an iron pot, B, containing a mixture of sodic nitrate and hydric sulphate, which react on each other, as already explained (par. 536, page 209), to form hydric nitrate. The vapours of sulphurous anhydride and hydric nitrate, together with excess of air, are conducted into a series of large leaden chambers, of which C represents one, and are there thoroughly mingled by jets of steam, supplied from a boiler, D. Hydric sulphate is formed in large quantity, and dissolves in the stratum of water with which the bottom of the chamber is covered.

753. The reaction which occurs is not very clearly ascertained, and probably several reactions take place simultaneously, according to the proportions in which the substances are mixed. But its general nature can be understood without

difficulty. The hydric nitrate is first decomposed by the sulphurous anhydride, with formation of nitric oxide and hydric sulphate. Thus,



Nitric oxide, as we have seen (par. 554, page 216), has a great affinity for free oxygen, and immediately takes it from the air which is admitted, passing into the condition of nitric peroxide.



This nitric peroxide is acted on by more sulphurous anhydride, which deprives it of some of its oxygen, and in presence of water forms more hydric sulphate, while nitric oxide again appears.



This nitric oxide is again oxidised, as expressed in equation (2), and thus the changes expressed in (2) and (3) alternate with each other continually.

754. In this way a small amount of nitric oxide theoretically suffices to convert a large quantity of sulphurous anhydride into hydric sulphate, provided abundance of atmospheric air be also present. It is the air, in truth, which supplies the oxygen requisite for the conversion of the one acid into the other; but sulphurous anhydride cannot directly take oxygen from atmospheric air, so as to change into hydric sulphate. The nitric oxide, accordingly, is essential, playing the part, as it were, of a carrier or go-between, alternately as nitric peroxide, yielding oxygen to the sulphurous anhydride, and returning as nitric oxide to procure a fresh supply from the air.

755. At intervals the liquid which condenses is drawn off from the floor of the leaden chamber. In this condition, it is not in a state of sufficient concentration for many purposes. It is deprived, accordingly, of the excess of water it contains, by heating it in shallow leaden troughs, or pans, to a temperature of about 160° , which expels water without dissipating any of the

hydric sulphate. The liquid is further concentrated in large vessels of platinum, till it acquires a density of 1.846 to 1.850. When of this specific gravity, it is a definite compound, expressed by the formula H_2SO_4 . It boils at 327° , and may be distilled without change.

756. *Properties.*—Hydric sulphate is a dense, oily, colourless, and odourless liquid. It is highly corrosive, as may be illustrated by letting a drop fall on paper or linen, which is rapidly destroyed by it. This corroding action is accompanied by a blackening or charring of the organic bodies on which it has acted, an effect which is owing to its separating the elements of water from the substance it chars, whilst it rejects the carbon, which appears with its characteristic black colour. This effect may be easily observed by leaving a splinter of wood for a few minutes in oil of vitriol. It has a strong, sour taste, which can be safely ascertained only with the diluted acid, and it reddens vegetable blues, and changes browns to yellows, like the other strong acids. It is, at ordinary temperatures, one of the most powerful of these bodies, displacing nearly every one of them from a state of combination. The process for preparing hydric nitrate was an illustration of the superiority in affinity for the strong bases of hydric sulphate over hydric nitrate.*

757. The great affinity of hydric sulphate for water has already been referred to. A bottle partially filled with the strong acid, if left unstoppered, will by and by run over, in consequence of the increase of volume occasioned by the water which it absorbs from the atmosphere. Advantage is taken of this property to dry substances which cannot be heated without undergoing decomposition. Organic substances, such, for example, as sugar or starch, may be totally deprived of moisture by reducing them to powder, and placing them in shallow saucers above a basin containing concentrated hydric sulphate.

* But much of this apparently strong affinity is due to its being comparatively non-volatile (par. 265, page 102). Even hydric borate, which is usually called a weak acid, and only volatilises at a red heat, can determine the production of hydric sulphate, when strongly heated with a sulphate.

The whole arrangement is covered by a bell-jar, to exclude the moisture of the outer air. Gases, moreover (those, at least, which do not act upon the acid), may be dried either by causing them to bubble through the liquid, or by passing them through a U-shaped tube filled with fragments of pumice-stone moistened with the strong acid.

758. When hydric sulphate combines with water, much heat is evolved, as may be ascertained by quickly mixing two parts of oil of vitriol with one of water in a glass flask. The vessel will, in a few seconds, become too hot to be held in the hand. A thin flask must be used for this purpose, as thick ones, owing to their slow and unequal conduction of heat, are very liable to be broken. In diluting the acid, therefore, for laboratory purposes, great care must be taken to add the acid *gradually* to the water, stirring the mixture continually.

759. Hydric sulphate is an example of a large class of salts, called SULPHATES, which may be derived from it by the replacement of the hydrogen which it contains by another basic radicle. In many cases, and especially when the acid is diluted, the hydrogen is evolved as gas—see, for instance, the preparation of hydrogen (par. 467, page 179); in other cases, as in the preparation of sulphurous anhydride (par. 742, page 295), by the action of the concentrated acid upon copper or mercury, a portion of the acid is decomposed. Many of these sulphates, as sodic sulphate and cupric sulphate, are of great importance in the arts, and will be referred to hereafter.

760. There are two classes of sulphates, derivable from hydric sulphate by the replacement of its hydrogen :

(1.) *Acid sulphates (bisulphates)*, in which one-half of the hydrogen is replaced. Thus, in the action of hydric sulphate on potassic nitrate (par. 536, page 209), we obtain at first a salt called hydric potassic sulphate, to which the formula KHSO_4 is assigned.

(2.) *Normal or Neutral sulphates*, in which the whole of the hydrogen is replaced. Thus, in the above reaction, when enough potassic nitrate is present, by raising the temperature

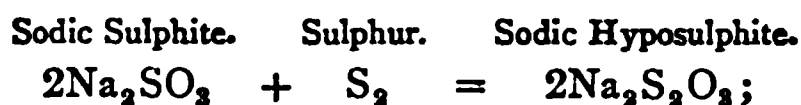
we obtain a salt of which the formula is K_2SO_4 . The relation of these salts will be more plainly seen when their formulæ are written as below.



761. We have, then, the same evidence in the case of hydric sulphate as in the case of water (hydric oxide), that its molecule contains *two* atoms of replaceable hydrogen. Acids (hydrogen salts) which agree in this particular with hydric sulphate, are classed together under the name of 'bibasic' acids. This will be referred to again under PHOSPHATES.

762. The best test for the presence of a sulphate in solution is a solution of baric chloride or nitrate. When a drop of this is added to a liquid containing a sulphate, a white precipitate of baric sulphate is formed, even in extremely dilute solutions. This precipitate is not soluble in ammonia or hydric nitrate.

763. There are several other series of compounds which appear to contain a radicle in which sulphur is associated with oxygen; but the only one of any practical importance is the class of *Hyposulphites*. Of this class, we shall take as an example sodic hyposulphite, a salt which is now manufactured in large quantities for the paper-maker and photographer, by boiling a solution of sodic sulphite with excess of sulphur. The following reaction takes place:



a molecule of the sulphite taking up an additional atom of sulphur. The salt crystallises in large colourless prisms, which are very soluble in water. It owes its importance in photography to the fact, that it readily decomposes argentic chloride and iodide, a soluble double salt of silver and sodium being formed. It is therefore used to dissolve out the unaltered silver salt from the parts of a picture which have not been acted on by light, and thus to 'fix' it (see under SILVER).

764. When a little dilute hydric sulphate is added to a solution of sodic hyposulphite, the liquid remains clear for a few moments, and then gradually becomes cloudy from a deposit of sulphur, while sulphurous anhydride is given off, and may be recognised by its smell. Hydric hyposulphite, which is at first formed, is very unstable, and decomposes into sulphur, water, and sulphurous anhydride. Again, when some solution of sodic hyposulphite is added to argentic nitrate, a precipitate is formed which is at first white, but rapidly becomes yellow, brown, and finally black. The explanation of this is, that argentic hyposulphite is very readily decomposed by water, forming hydric sulphate and black argentic sulphide.



The above reactions are quite sufficient for the detection of the hyposulphites.

HYDRIC SULPHIDE.

| | Formula. | Weight. | |
|---------------|----------------------|---------|---|
| Molecule..... | H_2S | 34 | 1 litre weighs 1.52 gm. Density = 1.175. |

COMPOSITION.

1 litre yields :

1 litre of hydrogen, weighing 0.0448 gm.
 $\frac{1}{2}$ a litre of sulphur, " 1.475 "

765. Sulphur forms with hydrogen an interesting and important compound, called hydric sulphide, besides a less important one called hydric persulphide, which need not be further alluded to. Hydric sulphide is evolved from volcanoes, and occurs in solution in many mineral springs, such as those of Harrogate, which owe their offensive smell and taste to the presence of the gas, derived probably from the decomposition of pyrites. It is produced during the decomposition of many animal and vegetable substances which contain sulphur. Thus the smell of rotten eggs is due to the gas, and it is produced in great quantity from sewage.

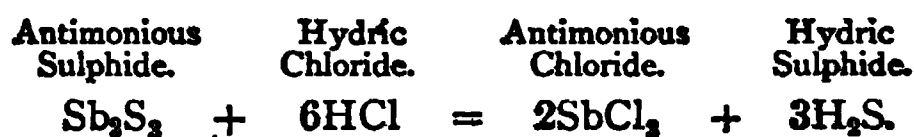
766. *Preparation.*—Hydric sulphide is prepared in the laboratory by the action of diluted hydric sulphate upon ferrous

sulphide. The formation of the latter substance has been already alluded to (par. 740, page 294). About 30 grms. of it, broken into small lumps, may be placed in a flask fitted with funnel and tube (see fig. 40), some water poured in, and then hydric sulphate (or chloride) added little by little, just as in the preparation of hydrogen. The gas should be collected over warm water, and not at a pneumatic trough coated with lead paint, or the latter will be blackened. From its poisonous and offensive properties, it must never be collected except in the open air, or in a good draught cupboard.

767. The evolution of the gas depends upon the following change. If iron alone be placed in the dilute acid, as we have already seen (par. 467, page 179), free hydrogen is evolved. If the iron be combined with sulphur, then the hydrogen which is produced comes off in union with the sulphur. Thus :



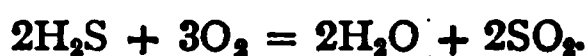
Another, and in some respects more convenient, method of preparing the gas, is to heat some powdered antimonious sulphide (common tersulphide of antimony) with strong hydric chloride. Any hydric chloride which may come over is retained by passing the gas through a small wash-bottle of water, B, fig. 73. The reaction is thus expressed :



768. *Properties.*—Hydric sulphide is a colourless gas, having the odour of rotten eggs. It does not support combustion, but is itself combustible. It is irrespirable, and a powerful poison. Water dissolves about two and a half times its volume of the gas, and acquires its offensive odour and taste. The class of mineral waters called sulphureous contain this gas in solution; only, however, in small quantity. It is a substance of great value to the chemist, as furnishing him with a most useful test for the distinction of metals, as well as other bodies, from each other. The following experiments may be tried with it:

(1.) A jar of the gas may be kindled, when it will burn with a blue flame, at the same time depositing some sulphur within the vessel.

(2.) If mixed with $1\frac{1}{2}$ time its volume of oxygen, and kindled, it burns with explosion, its hydrogen becoming converted into water, and its sulphur into sulphurous anhydride.



(3.) Mixed with an equal volume of chlorine, it is at once decomposed, and its sulphur separates, the chlorine combining with its hydrogen to form hydric chloride. Chlorine may be used in this way to purify apartments contaminated by the gas.

(4.) A silver coin, or a piece of paper soaked in a solution of plumbic acetate (sugar-of-lead), is at once blackened if placed in a jar of hydric sulphide. This effect depends upon the production of a metallic sulphide, by the combination of the sulphur of the gas with the silver or lead. This property of the gas causes it to act very injuriously on paintings containing any white-lead, and likewise on silver plate, and metallic utensils in general. Silversmiths, accordingly, are reluctant to burn coal-gas in their shops, because even the trace of hydric sulphide which escapes removal during the purification of the former, is sufficient to blacken and tarnish their goods. A white paint having the qualities of white-lead, but which hydric sulphide would not blacken, has long been a desideratum among artists, and the zinc paints do not entirely supply the want.

(5.) A solution of hydric sulphide may be prepared by allowing a current of the gas to stream through water for a short time. As this solution is continually used in the laboratory as a test, an engraving is given on the next page of the apparatus used for preparing it. The gas, generated in the flask A, is passed first through a small wash-bottle B, containing a little water, and then through two bottles, C, D, about three-fourths full of the water to be saturated with the gas. Any excess of gas is led through a tube into the open air or up a chimney. The solution must be pretty fresh for use in analysis, since

it is decomposed slowly by contact with air, water and sulphur being formed.

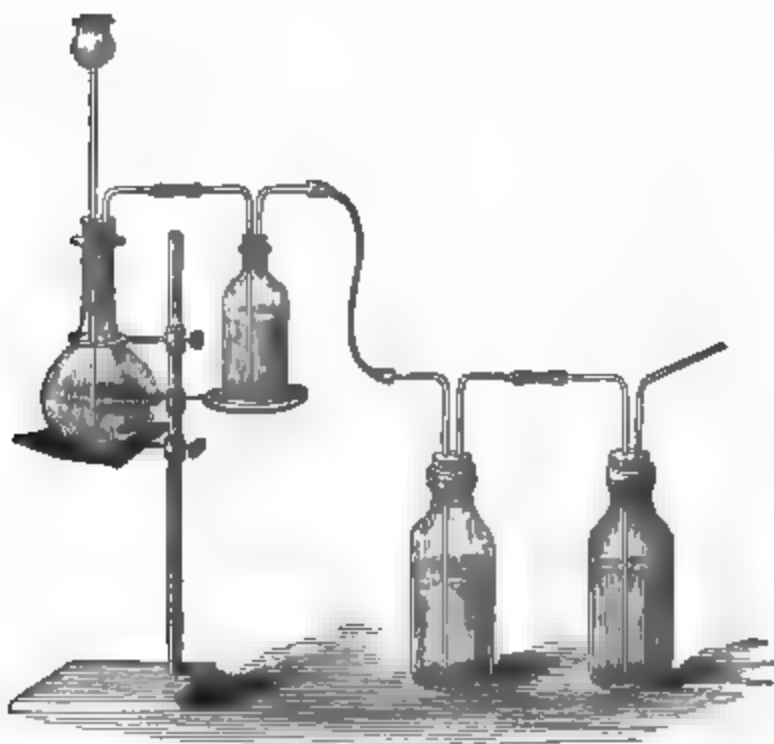


Fig. 73.

769. When a solution of hydric sulphide is added to a solution of a metallic salt, a sulphide or sulphydrate of the metal is formed. The analogy in composition of these substances to the oxides and hydrates must be noticed as only one of the many points of resemblance between sulphur and oxygen. Thus we have :

| | |
|-------------------------------|-------------------------------|
| Water, H_2O | Hydric sulphide, H_2S . |
| Potassic hydrate, KHO | Potassic sulphydrate, KHS . |
| Potassic oxide, K_2O | Potassic sulphide, K_2S . |
| Plumbic oxide, PbO | Plumbic sulphide, PbS . |

These compounds are in many cases characteristic from their colour, solubility, &c., and will be mentioned under the different metals. In the meantime, the following experiments will illustrate the value of hydric sulphide as a means of distinguishing the metals from each other, which is, however, only one of the modes in which it proves serviceable to the chemist.

770. A little fresh solution of hydric sulphide should be added to dilute solutions of the following salts, placed in test-glasses.

(1.) *Cupric sulphate*.—A black precipitate will be formed.

(2.) *Ferrous sulphate*.—A black precipitate will here also be formed.

If a little dilute hydric chloride is added to each, the cupric sulphide will remain unaltered, while the ferrous sulphide will dissolve readily, the solution becoming colourless.

(3.) *Arsenious anhydride*. (*white arsenic*).—A yellow precipitate will be obtained, insoluble in hydric chloride.

(4.) *Zinc sulphate*.—A white precipitate, if the solution is neutral, soluble in hydric chloride.

(5.) *Calcic chloride*.—No precipitate, calcic sulphide being soluble in water.

The importance of the properties of these sulphides in classifying the metals will be explained in the introductory part of the chapter on Metals.

CARBONIC DISULPHIDE.

| | Formula. | Weight. | Density of vapour = 2.67. |
|---------------|-----------------|---------|---------------------------|
| Molecule..... | CS ₂ | 76 | " liquid = 1.27. |

771. This substance is prepared in considerable quantities by the direct union of its elements. The vapour of sulphur is driven over fragments of charcoal heated to redness in a tube or retort of porcelain, and the liquid product is condensed in a carefully cooled receiver.



772. Carbonic disulphide is a very volatile, colourless fluid, with an unpleasant odour. It refracts light strongly, and is hence used for filling prisms for spectrum analysis (Chapter VI.). It boils at 47°, giving off a highly inflammable vapour, so that great care is necessary in dealing with it. The products of its combustion in air are sulphurous anhydride and carbonic

dioxide. It is insoluble in water, and sinks to the bottom of a jar of water owing to its high density. It is chiefly used in the arts for dissolving substances; india-rubber, sulphur, phosphorus, iodine, and many oils and fats dissolving readily in it. Its analogy to carbonic dioxide will be seen from its formula, and is further shewn by its forming salts (sulphocarbonates) corresponding to the carbonates, but containing sulphur in place of oxygen.

SELENIUM.

| | Symbol. | Weight. | |
|---------------|-----------------|---------|---|
| Atom..... | Se | 79.5 | 1 litre weighs 7.025 grms. Density of solid = 4.3. |
| Molecule..... | Se ₂ | 158 | |

773. Selenium is a rare substance, closely resembling sulphur in properties, and occurring in nature associated with it in pyrites and in combination with lead as plumbic selenide. Its name is derived from the Greek *σελήνη* (*Selené*), the moon, in allusion to its similarity in properties to the element *Tellurium*, which receives its name from the Latin *tellus*, the earth. It is chiefly obtained from the residues of manufactories near Fahlun, in Sweden, where seleniferous pyrites is used in the preparation of sulphuric acid.

774. Selenium is so rare and costly, that the student will not have it in his power to try experiments with it. We mention, therefore, its properties exceedingly briefly. At ordinary temperatures it is a solid, of a brownish-red colour, semi-transparent, and with a lustre somewhat resembling that of the metals. It melts a little above 200°, and boils below a red heat, forming a yellow vapour paler than that of sulphur.

775. It forms combinations analogous to those of sulphur in composition and properties. Thus, we have:

| | | |
|---|------------------|---|
| Selenious anhydride, SeO ₂ , | corresponding to | sulphurous anhydride, SO ₂ . |
| (Selenic " SeO ₃ , | " | sulphuric " SO ₃). |
| Hydric selenideH ₂ Se, | " | hydric sulphide.....H ₂ S. |

776. Selenious anhydride, unlike sulphurous anhydride, is

a solid body, easily obtained in crystals by heating selenium in hydric nitrate, and driving off the excess of acid by heat. It dissolves in water, forming hydric selenite, from which a series of salts, called selenites, are derivable.

777. Selenic anhydride has not been yet obtained; but hydric selenate (H_2SeO_4), corresponding to hydric sulphate (H_2SO_4), is known. Potassic selenate is procured by fusing selenium with nitre. It is a powerful acid, and has one property possessed by no other simple acid—that, namely, of dissolving gold, although platinum is not acted on by it.

778. It unites with hydrogen to form hydric selenide, a colourless gas, obtained by heating selenium in moist air. It has a peculiar disagreeable odour, compared to that of decaying horse-radish, the development of which before the blow-pipe flame enables us to recognise selenium in bodies containing it. This gas, if respired even in very small quantity, produces excessive irritation of the lining membrane of the nostrils and air-tubes of the lungs, so that it has even been conjectured by an eminent chemist that our epidemic influenza may be occasioned by the evolution of this gas from volcanoes, and its consequent presence in the atmosphere.

779. None of the compounds of selenium, nor the element itself, are used in the arts.

TELLURIUM.

| | Symbol. | Weight. | |
|---------------|---------------|---------|--|
| Atom..... | Te | 129 | 1 litre of vapour weighs 11.535 grms. |
| Molecule..... | Te_2 | 258 | |

780. This element is of very rare occurrence, and is interesting as forming a link between the non-metals and the metals, being in some of its properties analogous to selenium, in others to antimony. It is found in Hungary and in Virginia in combination with gold and bismuth.

781. Tellurium is a brittle crystalline substance with a metallic lustre like antimony. It melts at about 500° , and volatilises at a high temperature. It forms two oxides, TeO_2

and TeO_3 , and these combine with water to form hydric tellurite, H_2TeO_3 , and hydric tellurate, H_2TeO_4 , respectively. It also forms a compound with hydrogen, H_2Te , closely resembling hydric sulphide in smell and other properties.

ANALOGIES OF THE SULPHUR GROUP.

782. Sulphur, selenium, and tellurium form a group of elements no less closely connected than the members of the chlorine group. Oxygen must be considered as belonging to the same group, but standing (like fluorine) somewhat apart from the rest. The following table will indicate a few of the points of analogy :

| | Sulphur. | Selenium. | Tellurium. | Oxygen. |
|------------------------------|-------------------------------|-------------------------------|-------------------------------|------------------------|
| (A.) | | | | |
| Condition..... | Solid, fuses at 114° . | Solid, fuses at 212° . | Solid, fuses at 500° . | Gas. |
| Appearance..... | Yellow. | Brown - red, semi-metallic. | Metallic lustre. | Colourless. |
| Density of solid... | 2.0. | 4.3. | 6.2. | ? |
| (B.) | | | | |
| Atomic weight.... | 32. | 79.5. | 129. | 16. |
| Compounds with oxygen..... | SO_2 . | SeO_2 . | TeO_2 . | |
| | SO_3 . | (SeO_3) . | TeO_3 . | |
| Compounds with hydrogen..... | H_2S . | H_2Se . | H_2Te . | H_2O . |
| | Fetid, poisonous gas. | Fetid, poisonous gas. | Fetid, poisonous gas. | Neutral liquid. |

Section VII.—Triatomic Elements: Phosphorus, Boron.

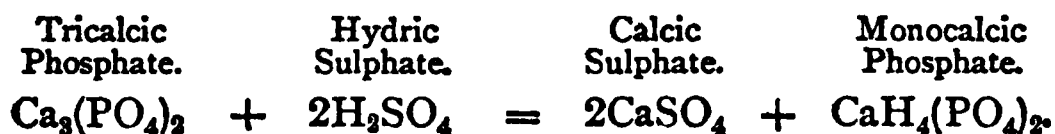
PHOSPHORUS.

| | Symbol. | Weight. | |
|---------------|--------------|---------|----------------------------|
| Atom..... | P | 31 | 1 litre weighs 5.542 grms. |
| Molecule..... | P_4 | 124 | Density of vapour = 4.284. |

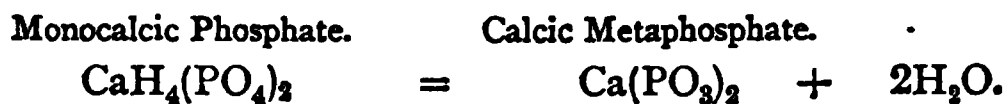
783. *Distribution.*—Phosphorus occurs chiefly in combination with oxygen, calcium, and magnesium, in volcanic and other rocks, which, by crumbling down, form our fertile soils. It is

a never-failing constituent of the plants used by man and the domesticated animals as food—such as grains, peas, and beans ; in which it occurs both in the forms of calcareous phosphates, and in a peculiar state of combination with carbon, oxygen, hydrogen, and nitrogen. It is an equally characteristic and important ingredient of animal structures. Their bony skeletons owe their strength and rigidity to calcic and magnesian phosphates ; whilst phosphorus exists in other states of combination in the flesh, blood, brain, milk, and other tissues and secretions of animals.

784. *Preparation.*—Different processes are followed in the preparation of phosphorus, but the simplest is the following : Bones are burned to whiteness in an open fire, ground to powder, and mixed with hydric sulphate somewhat diluted. The whole is well stirred, and left at rest for some hours. At the end of this time fresh water is added, and the liquid passed through a filter. The change which takes place is the following : Bone-earth consists of an insoluble salt containing calcium, phosphorus, and oxygen (tricalcic phosphate). Part of the calcium is withdrawn by the action of the acid, forming insoluble calcic sulphate ; while the rest forms a very soluble monocalcic phosphate (the ordinary ‘superphosphate of lime’).



The solution which passes through the filter, and which contains all the phosphorus, originally present in the bones, is evaporated to the consistence of a syrup, mixed by stirring with powdered charcoal, and heated in an iron vessel until every trace of water is expelled. The monocalcic phosphate gives off the elements of water, passing into another modification, called calcic metaphosphate. Thus :



This last salt, unlike the other calcic phosphates, is capable

of being decomposed by carbon at a higher temperature, and forms phosphorus, carbonic oxide, and tricalcic phosphate.



The dried mass is introduced into a retort made of fire-clay, which is placed in a furnace and raised to a white heat. From the mouth of the retort a wide copper tube proceeds, which is bent at right angles, and dips below the surface of water contained in a glass vessel. The carbonic oxide escapes by the bent tube, and bubbles up through the water; whilst the phosphorus, rising in vapour, and descending into the water, condenses there.

785. In order to purify the crude product, it is melted a second time under the surface of a solution of potassic dichromate in dilute hydric sulphate, filtered by pressing it through wash-leather, and cast in cylindrical moulds, so that it is met with in commerce in the form of sticks, somewhat like those of barley-sugar.

786. *Properties.*—Phosphorus is, at ordinary temperatures, a soft, transparent, pale-yellow solid, resembling beeswax in consistence, and admitting of being cut or moulded like it. It is insoluble in water, under which it is kept to prevent its spontaneous combustion. It dissolves in the volatile oils, in naphtha, carbonic disulphide, &c., and may be obtained from these solutions in crystals, which are not, however, easily preserved. It melts at 42° , and boils at 288° , beginning to rise in vapour a little above the temperature of boiling water. To observe these phenomena, a small piece of carefully dried phosphorus should be placed at the bottom of a long narrow tube sealed at one end. On heating this, the solid will be observed to melt, form an amber-yellow, highly transparent liquid, evolve a pale-yellow vapour, and finally boil. If a wide tube be taken, the phosphorus takes fire, and the phenomena in question are not observed, unless the tube is previously filled with carbonic dioxide, by displacement.

787. The most remarkable property of this substance is its

excessive inflammability, and the intense light and heat which it evolves when burning. From this character it has received its name from two Greek words, signifying, in combination, the *light-bringer*, or *light-producer*, being the exact equivalent of the Latin compound *lucifer*. Its inflammability may be well shewn by pouring a few drops of solution of phosphorus in carbonic disulphide upon a piece of blotting-paper. As the solvent evaporates, the phosphorus is left in a finely divided condition, and almost immediately takes fire.

788. Phosphorus takes fire spontaneously in warm weather, and at all ordinary temperatures is readily kindled by friction, a stroke, or the heat of the hand. It must therefore be handled cautiously. It is luminous in the dark; as may be observed by placing a stick in a jar of air, or using it, like a crayon, to write or draw with on a wall. In employing it thus, the phosphorus should not be kept long dry, or held in the naked fingers. It may be dipped at intervals into a vessel of water. When phosphorus is thrown into a jar containing hot water, and a stream of oxygen from a gas-holder directed upon it, the phosphorus burns vividly under the surface of the water. A similar combustion in a chlorine oxide has been already mentioned (par. 684, page 271).

789. Phosphorus can be obtained in at least one other allotropic form. This is called 'red' or 'amorphous' phosphorus, and may be prepared by heating dry ordinary phosphorus in a sealed tube or a flask filled with carbonic dioxide to a temperature of 230° in an oil-bath for several days. It is also formed in small quantity when phosphorus is burned in air or oxygen. Another method of obtaining it is, to add a minute fragment of iodine to phosphorus, heated, in an atmosphere of carbonic dioxide, a little above its melting-point. The whole mass is suddenly converted into the allotropic form, with evolution of much heat. Red phosphorus, however prepared, retains traces of ordinary phosphorus, which are separated by digesting the powdered mass with carbonic disulphide.

790. These two varieties of phosphorus, although chemically identical in composition, differ much in properties. 'Amorphous' phosphorus is a hard, brittle, red substance, which may be handled with impunity, and may be heated in air or oxygen much above the boiling-point of water, without fusion or alteration. At a temperature of 260° , however, it is suddenly reconverted into ordinary phosphorus, and bursts into flame. The conversion may be watched by heating a little amorphous phosphorus in a tube filled with carbonic dioxide, when it sublimates without fusion, and condenses in amber drops of ordinary phosphorus.*

791. When phosphorus is exposed to the action of light under water it turns red, and becomes coated with a white opaque film, which appears to be another variety of the element.

792. The principal use of phosphorus is in the manufacture of lucifer matches. If a *very small* piece of phosphorus (either ordinary or amorphous) is placed in contact with a little powdered potassic chlorate, and then struck with a hammer, it is oxidised, and bursts into flame with explosion. The ends of matches, after being dipped in melted paraffine, are coated with a mixture of phosphorus and potassic chlorate made into a paste with gum, a little sand being added to increase the friction. Such matches ignite on being rubbed on any rough surface, and many accidents have happened from their careless use. Moreover, the manufacture of them is highly dangerous, not only from the inflammable materials used, but also from the poisonous nature of the vapour of ordinary phosphorus, which occasions serious and fatal disease among the workmen. Improvements have been recently introduced, which consist, firstly, in the use of amorphous instead of ordinary phosphorus, secondly, in the separation of the oxidising agent from the phosphorus until the moment when a light is wanted. The so-called 'safety' matches are tipped with a mixture of potassic chlorate and antimonious sulphide, materials which have no

* It is remarkable, however, that the red phosphorus obtained by the iodine process volatilises unaltered—probably on account of the presence of a trace of iodine.

tendency to ignite until strongly heated. The 'rubber' upon the box is coated with a layer of amorphous phosphorus and antimonious sulphide, an equally harmless mixture. When the match is rubbed upon this prepared surface, a sufficient number of particles of phosphorus and potassic chlorate come in contact to cause inflammation.

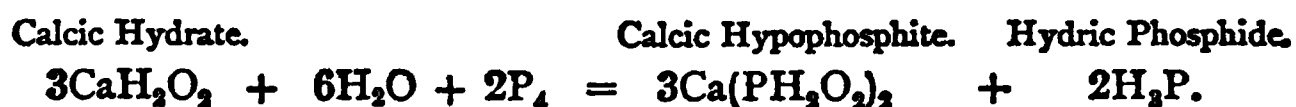
793. The compounds formed by phosphorus with other radicles are called PHOSPHIDES. Few of them are of any special interest. An impure calcic phosphide is formed when the vapour of phosphorus is passed over red-hot quicklime. To obtain it, a few pieces of phosphorus are placed at the sealed end of a piece of infusible tubing ('combustion' tube) about 40 cm. long, and the rest of the tube filled with fragments of quicklime. It is then placed in a furnace nearly horizontally, the closed end containing the phosphorus being a little lower than the other, and projecting slightly from the furnace. When the lime is at a low red-heat, the phosphorus is cautiously heated to boiling by a spirit-lamp. The lime glows brightly as the vapour reaches it, and a dark-brown substance is formed, which is probably a mixture of calcic phosphide (Ca_2P_2) and calcic phosphate. This body should be preserved in a closely stoppered bottle, since, as will be described in the next paragraph but one, it is decomposed by moisture, with production of hydric phosphide.

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.

794. Phosphorus appears to form three compounds with hydrogen—a solid (HP_2), a liquid (H_4P_2), and a gas (H_3P). The last, which is analogous in composition to ammonia (H_3N), is the only one which need be described.

795. When fragments of the calcic phosphide, described above, are dropped into water, bubbles of a gas are given off, which burst into flame as they reach the surface, producing beautiful white wreaths of hydric phosphate, and exhaling a strong offensive garlic-like odour. This gas is hydric phosphide,

or phosphamine as it is termed, to indicate its analogy to ammonia. Instead of taking calcic phosphide, a more convenient process for preparing the gas is to heat phosphorus with lime and water in a small retort. The experiment is scarcely a safe one for an inexperienced beginner, but it may be successfully made as follows: About half a gramme of phosphorus is to be placed in a small non-tubulated retort, holding about 100 c.c. The retort is then to be completely filled with milk of lime, made by shaking up with water 6 or 8 grms. of slaked lime (calcic hydrate),* and supported in a firm holder, so that its beak may dip some little way under the surface of water in a trough. On slowly applying heat, the following action takes place:



The water is decomposed; part of its hydrogen unites with phosphorus to form hydric phosphide, while the rest, with the elements of calcic hydrate, combines with more phosphorus to form a salt called calcic hypophosphite, which will be alluded to again presently. The gas collects in the arch of the retort, and soon displaces all the liquid, and bubbles up through the water in the trough. Thus no air enters the retort, and the gas cannot burn till it has escaped from the beak of the retort, and risen into the external air.

796. The preparation of phosphuretted hydrogen is one of the most beautiful experiments in chemistry. Each bubble of gas, when it reaches the surface of the water into which the beak of the retort dips, bursts into flame, and changes into a ring or wreath of white smoke, consisting of hydric phosphate.



These rings ascend in the air, widening as they rise, and presenting a very curious combination of movements. The

* A much better material is baric hydrate (baryta) if it can be procured, since it is much more soluble in water than calcic hydrate. Caustic potash may be used, but the gas obtained is, owing to a secondary action, diluted with a large quantity of pure hydrogen.

whole ring increases in diameter horizontally, whilst it appears to present a series of internal revolutions in a vertical direction, as if made up of a multitude of smaller rings, placed at right angles to the plane or direction of the large one, and each revolving vertically, whilst the great circle expands horizontally. These circles are produced by the sudden expansion of the film of hydric phosphate, caused by the heat of combination.

797. If bubbles of phosphuretted hydrogen are allowed to ascend into a jar half full of air or oxygen, standing on the pneumatic trough, a flash of light is seen within the jar when the gases meet. The experiment is striking, but requires to be cautiously performed when oxygen is employed. Not more than one bubble of hydric phosphide should be allowed to ascend at a time. The jar must be strong and thick, and should be grasped firmly in the hand, to prevent its being thrown over by the concussion which attends the explosive combustion of the gases. When the experiment is over, the retort should be allowed to cool, and then, its beak still remaining under water, it should be wholly immersed in the trough, and water allowed to enter, in order to displace the remaining gas.

798. Hydric phosphide, as thus prepared, has a strong, most offensive odour, and is highly poisonous. It is sparingly soluble in water, and when passed through a solution of a gold or silver salt, causes a precipitate of the metal. Although it has no alkaline reaction, it shews in many other respects a close analogy to ammonia. Thus, it unites with hydric iodide to form a salt which crystallises in cubes, and much resembles ammoniac iodide. Its most characteristic property, its spontaneous inflammability in air, has been sufficiently described. This is believed to be due to the presence of traces of the liquid hydric phosphide (H_4P_2), and it may be deprived of this property by passing it over charcoal, by mixing it with vapour of ether, or by cooling in a freezing mixture the tube through which it passes. Hydric phosphide may be obtained in a state of purity by heating hydric phosphite (see par. 802), and

when thus prepared it does not spontaneously inflame; but, if a small quantity of nitric oxide gas is added, the gas acquires the characteristic inflammability of the ordinary variety.

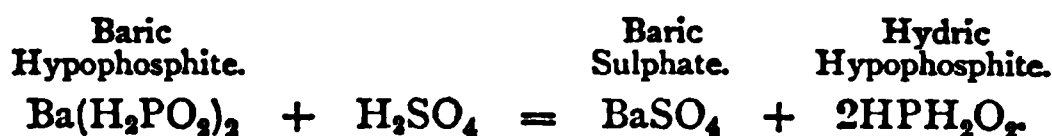
COMPOUNDS OF PHOSPHORUS WITH OXYGEN AND HYDROGEN.

799. There are only two well-defined, isolable, phosphorous oxides:

Phosphorous Anhydride..... P_2O_3
 Phosphoric Anhydride..... P_2O_5

The existence of a third, the formula of which would be P_2O , is rendered probable, since hydric hypophosphite may be regarded as formed by the combination of such an oxide with water ($P_2O + 3H_2O = 2HPH_2O_2$). This substance will therefore be first described.

800. *Hydric Hypophosphite*.—It has already been observed that, when phosphorus is boiled with calcic hydrate and water, a salt called calcic hypophosphite is formed. A similar salt, baric hypophosphite, is obtained by using baric hydrate instead of calcic hydrate; and when it is dissolved in water, and hydric sulphate added as long as a precipitate is formed, a solution of hydric hypophosphite is procured.



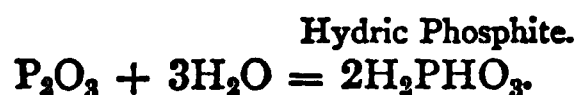
The solution may be evaporated down to a strongly acid, syrupy liquid; but, when further heated, it decomposes into hydric phosphate and hydric phosphide, which latter takes fire. Only one atom of the hydrogen in this acid is replaceable by other basic radicles, and hence its formula should be written HPH_2O_2 , to express the fact that some of the hydrogen is in a state of combination different to the rest. The class of **HYPOPHOSPHITES** which are thus formed are, from their tendency to pass into phosphates, powerful reducing agents. Thus, when a solution of calcic hypophosphite is added to a solution of

argentic nitrate, the white precipitate at first formed quickly turns brown, owing to its reduction to metallic silver.

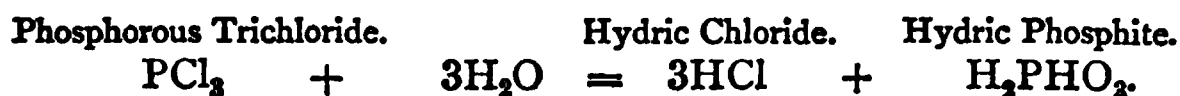
PHOSPHOROUS ANHYDRIDE.

| | Formula. | Weight. |
|---------------|----------|---------|
| Molecule..... | P_2O_3 | 110 |

801. This is the least interesting of the compounds of phosphorus. It may be prepared by burning phosphorus in a limited supply of air. In illustration of this, a tube of glass should be taken about 40 cm. in length and 1 cm. in diameter. It is to be bent close to one extremity at an obtuse angle, and the shorter limb drawn out at the blow-pipe into a conical shape, so as to leave an aperture not larger than would admit a pin's point. Into the tube, held obliquely with the bent end lowest, and the capillary tube pointing upwards, a small fragment of dry phosphorus is to be introduced, and allowed to slide down into the angle. When the tube is heated at this point, the phosphorus takes fire, and burns with a pale greenish flame; but owing to the small quantity of air which reaches it through the narrow aperture; it forms; only phosphorous anhydride, which is carried along with the heated air, and condenses in the upper part of the tube as a soft, white, readily volatile powder, which combines with water, forming hydric phosphite.



802. Hydric phosphite is practically obtained by the decomposition of phosphorous trichloride (par. 813) by water, which is expressed in the following equation :



The liquid is warmed till the whole of the hydric chloride has escaped as gas, and has left a pure solution of hydric phosphite. This acid is interesting chiefly as a source of pure hydric

phosphide, which it yields when its aqueous solution is concentrated in a retort. Thus :



Two out of the three atoms of hydrogen are replaceable by basic radicles, a series of salts, called PHOSPHITES, being formed, which, like the hypophosphites, readily absorb oxygen, and pass into phosphates.

PHOSPHORIC ANHYDRIDE.

| | Formula. | Weight. |
|---------------|------------------------|---------|
| Molecule..... | P_2O_5 | 142 |

803. This, which is the highest phosphoric oxide, and corresponds to nitric anhydride (N_2O_5), is prepared by burning phosphorus in excess of air or oxygen. Its formation may be shewn by setting fire to a piece of phosphorus lying on a stoneware plate, or sheet of metal, and covering the combustible after it is lighted with a bell-jar. The phosphorus combines with the oxygen of the air to form phosphoric anhydride, which ascends in the current of hot air as a thick, white smoke, and as the whole cools, falls upon the plate as a soft white solid, scarcely distinguishable from snow in appearance. Oxygen may be taken instead of air, but is not necessary. Whilst discussing the former gas, we have described the mode in which phosphorus may be burned in it.

804. The snow-like phosphoric anhydride absorbs moisture with great rapidity from the air, and runs into a liquid. When dropped into water, it hisses like red-hot iron quenched in that fluid, owing to the high temperature produced when it combines with it. The compound which is formed at first is chiefly hydric metaphosphate, corresponding to hydric nitrate :



When, however, the solution is boiled, more water is taken up, and eventually a solution of hydric orthophosphate is obtained.

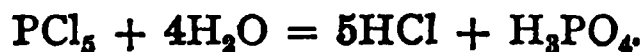
805. *Hydric Phosphates*.—Phosphoric anhydride may be

combined with water in several proportions, forming perfectly distinct acid substances. Thus we have :

- (1.) $P_2O_5 + H_2O = 2HPO_3$, Hydric Metaphosphate.
- (2.) $P_2O_5 + 2H_2O = H_4P_2O_7$, Hydric Pyrophosphate.
- (3.) $P_2O_5 + 3H_2O = 2H_3PO_4$, Hydric Orthophosphate.

Of these the last is the most stable, and is the substance into which the others are converted when in solution in water, especially if their solutions are boiled. It will therefore be described first.

806. *Hydric Orthophosphate*.—This acid is formed when phosphoric pentachloride is decomposed by water (compare the decomposition of phosphorous trichloride, par. 813).



It is usually prepared either by decomposing bone-earth (calcic phosphate) by excess of hydric sulphate, or by boiling phosphorus with moderately dilute hydric nitrate, and evaporating the solution to a syrup. It has a pleasant, strongly sour taste, and reddens litmus powerfully. It is not directly poisonous, nor very corrosive, and is used as a medicine; but from its property of dissolving calcic phosphate, it acts destructively on the teeth; and hence, when administered, it must be sucked through a quill or glass tube.

807. Each of the three atoms of hydrogen in the acid may be replaced by a basic radicle, and hydric orthophosphate is therefore a good example of a *tribasic* acid. We have already had examples of other acids of different basicity—for instance, hydric nitrate (HNO_3), a monobasic acid, and hydric sulphate (H_2SO_4), a bibasic acid—and it has been explained that the basicity of an acid depends upon the number of atoms of replaceable hydrogen which its molecule contains. Now, from hydric orthophosphate, we can derive three series of salts, called ORTHOPHOSPHATES, and we may take as examples the salts obtained by the replacement of its hydrogen by sodium.

808. (1.) When a solution of hydric orthophosphate is exactly neutralised by the addition of sodic carbonate, the

liquid, on evaporation, yields crystals in the form of oblique rhombic prisms. These consist of a salt in which two out of the three atoms of hydrogen in the acid are replaced by two atoms of sodium, its formula being Na_2HPO_4 . It is called disodic hydric orthophosphate (the common 'rhombic phosphate of soda').

(2.) When this salt is mixed with an excess of sodic hydrate, a crystallisable salt, in which all the three atoms of hydrogen of the acid are replaced by sodium, is obtained. Its formula is Na_3PO_4 , and it is called trisodic orthophosphate.

(3.) On the other hand, if any quantity of hydric orthophosphate is divided into two halves, the one half neutralised with sodic phosphate, and then the other half added, a different salt is obtained in which only one of the atoms of hydrogen in the acid is replaced. The name of this salt is sodic dihydric orthophosphate, and its formula, NaH_2PO_4 . The relation between these salts will be plain from the table below :

| | |
|-----------------------------|-----------------------------|
| Hydric Orthophosphate | H_3PO_4 . |
| Sodic Dihydric " | NaH_2PO_4 . |
| Disodic Hydric " | Na_2HPO_4 . |
| Trisodic " | Na_3PO_4 . |

809. Tests for the Orthophosphates.

(1.) When a solution of argentic nitrate is added to any soluble orthophosphate, a yellow precipitate of triargentic orthophosphate is formed, which readily dissolves both in dilute hydric nitrate and in ammonia.

(2.) On addition of excess of ammonia, and then of a drop or two of solution of magnesian sulphate, a white granular precipitate of magnesian ammoniac phosphate, $\text{Mg}''(\text{H}_4\text{N})\text{PO}_4$, is formed.

(3.) When a few drops of solution of an orthophosphate are added to a solution of ammoniac molybdate in hydric nitrate, a yellow precipitate is obtained. This is a most delicate test.

810. *Hydric Pyrophosphate*, $\text{H}_4\text{P}_2\text{O}_7$.—This may be obtained by carefully heating the orthophosphate until a certain quantity of water is driven off. A salt belonging to the same series,

sodic pyrophosphate, may be readily procured in a state of purity by heating to redness some disodic hydric orthophosphate, two molecules of the salt giving off one molecule of water, thus :



The salt thus obtained may be taken as a type of the pyrophosphates. A little of it may be dissolved in *cold* water, and tested as above.

(1.) With argentic nitrate, a white granular precipitate will be formed.

(2.) With magnesian sulphate, after addition of ammonia, a crystalline precipitate of magnesian pyrophosphate will be formed.

(3.) With ammoniac molybdate, no precipitate is obtained. Hydric pyrophosphate is tetrabasic, forming four series of salts.

811. *Hydric Metaphosphate*, HPO_3 .—This substance, as above mentioned, is the product of the first action of phosphoric anhydride on water. Sodic metaphosphate may be obtained by a process similar to that for obtaining the pyrophosphate, namely, by heating sodic dihydric orthophosphate, or any other orthophosphate containing only one atom of a non-volatile basic radicle, thus :



Instead of the above, the salt called 'microcosmic salt,' which is an orthophosphate containing sodium, ammonium, and hydrogen ($\text{Na}(\text{H}_4\text{N})\text{HPO}_4$), and which is readily procured, may be heated to redness in a small platinum capsule. It gives off water and ammonia, and leaves a transparent glassy residue of sodic metaphosphate. This may be dissolved in cold water, and tested in the same way as the other salts.

(1.) With argentic nitrate, metaphosphates give a white gelatinous precipitate, soluble in excess of the metaphosphate.

(2.) With magnesian sulphate, no precipitate is formed.

(3.) With ammoniac molybdate, no precipitate.

(4.) If a little of the solution is added to a clear solution of

albumen, strongly acidified with hydric acetate (acetic acid), a white precipitate of coagulated albumen is formed. This effect is not produced either by pyrophosphates or by orthophosphates. Hydric metaphosphate is a monobasic acid forming only one series of salts.

812. It is observable that when a solution of hydric pyrophosphate or metaphosphate is boiled for some time, it combines with more water, and passes into the state of orthophosphate, which may be recognised by the usual tests.

COMPOUNDS OF PHOSPHORUS WITH CHLORINE AND IODINE.

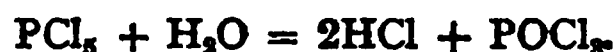
813. Phosphorus unites directly with chlorine, as we have already seen, melting and catching fire when introduced into the gas. It forms two definite chlorides—the trichloride (PCl_3), and the pentachloride (PCl_5), which are of great importance in organic chemistry as means of procuring new compounds.

(1.) Phosphorous trichloride is formed by passing a stream of dry chlorine over phosphorus heated gently in a retort. A volatile, colourless liquid distils over, which boils at 74° , and fumes in moist air. When dropped into water it sinks to the bottom and quickly decomposes into hydric chloride and hydric phosphite (see par. 802, page 321).

(2.) Phosphoric pentachloride is formed by acting upon phosphorus with chlorine in excess. It is most readily prepared by passing a rapid stream of chlorine into a flask containing the trichloride. The gas is quickly absorbed, and the contents of the flask solidify into a mass of yellow crystals which are the pentachloride. These crystals sublime at 100° without previous fusion; and it is noticeable that the vapour has a density almost exactly one-half that which analogy leads us to assign to a body of which the molecular formula is PCl_5 .* Phosphoric

* The density of phosphoric pentachloride at 336° is 3.656 (air = 1). Hence 1 litre of its vapour weighs ($3.656 \times 1.293 =$) 4.727 grms. Now, this is only 52.5 times the weight of a litre of hydrogen, whereas, on the hypothesis that the weights of equal volumes of gases are in the same ratio as the weights of their molecules (par. 380, page 144), a molecule

pentachloride acts upon water, when the latter is in excess, in a way similar to the trichloride, forming hydric chloride and phosphate. But when only a small quantity of water is brought in contact with it, a substance called phosphoric oxychloride (POCl_3) is produced :



814. Phosphorus has scarcely less affinity for iodine than for chlorine. Two phosphorous iodides are known—the di-iodide (PI_2), and the tri-iodide (PI_3). An experiment, shewing the direct combination of the elements, has been already given (par. 718, page 284); but, in order to obtain the definite compounds, it is best to dissolve the phosphorus and iodine, in the proportions indicated by the formulæ, in carbonic disulphide, and then to mix the solutions, and cool the liquid until it deposits crystals. Phosphoric di-iodide crystallises in orange-red prisms; phosphoric tri-iodide in dark-red hexagonal plates. Both these iodides are decomposed by water, yielding hydric iodide and hydric phosphite (see par. 708, page 280).

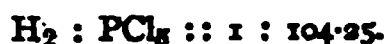
815. Phosphorus forms several compounds with bromine and with sulphur, but they are of no great importance.

BORON.

| | Symbol. | Weight. | Density of diamond boron = 2.63. |
|---------------|--------------|---------|----------------------------------|
| Atom..... | B | 11 | |
| Molecule..... | B_2 | 22 (?) | |

816. Boron is an element which, although, from the composition of its chloride, it appears to belong to the triatomic group, has greater analogies to carbon and silicon than to phosphorus or nitrogen. It is not abundantly found in nature, and the supply is mainly derived from two sources.

with the formula PCl_5 , ought to weigh 104.25 times as much as the hydrogen molecule H_2 ; since



This anomaly has been explained, by supposing that at the high temperature of 336° the molecule of pentachloride is decomposed into a molecule of trichloride and a molecule of chlorine, the system thus occupying twice as much space as before (see pages 154, 155).

(1.) Its combination with hydrogen and oxygen, hydric borate or 'boric acid,' which is found in the jets of steam, called *fumarolles*, issuing from the earth in the volcanic districts of Tuscany. Round the fissures from whence these jets issue, basins are constructed, and kept full of water, in which the steam and hydric borate are condensed; while the heat evaporates the solution, which is drawn off, and further concentrated, until it deposits crystals of hydric borate on cooling.

(2.) Its combination with sodium and oxygen, sodic borate, called 'tincal,' or 'rough borax,' which is found in certain salt lakes in Tibet and California.

817. The element boron is not easy to prepare, and has been applied to no practical use. It owes its chief interest to the fact that it can be obtained in at least three allotropic forms, resembling those of carbon. It is prepared by heating its oxide (par. 818) with metallic sodium, in an iron crucible. The sodium combines with the oxygen, and boron is separated as a dark-brown amorphous powder, insoluble in water, and otherwise resembling lampblack in physical properties. When aluminium is used instead of sodium, the boron appears to dissolve in the metal, like carbon in iron, and separates, as the mass solidifies, in the form of dark-brown scales, like graphite. It may also be obtained, by repeated fusion with aluminium, in crystals, which are almost as hard as the diamond.

COMPOUNDS OF BORON.

818. Boron forms only one combination with oxygen, boric trioxide, or anhydride (B_2O_3), corresponding in composition to phosphorous anhydride (P_2O_3). It is prepared by strongly heating hydric borate, which melts, gives off water, and leaves a transparent, colourless, glassy mass, consisting of the trioxide.



819. *Hydric Borate*.—This acid, which is the result of the combination of boric trioxide with water, is prepared in a pure

state either by recrystallising the crude product obtained from Tuscany (see par. 816), or by adding the proper proportion of strong hydric sulphate to a hot saturated solution of sodic diborate (borax). The reaction consists essentially in the exchange of sodium for hydrogen ; thus :



The hydric borate, being sparingly soluble in cold water, crystallises in thin pearly scales, as the liquid cools.

820. The decomposition of hydric borate by heat has been mentioned in par. 818. Its taste is only faintly sour, and it does not fully redden litmus, but turns it to a purple tint, like carbonic dioxide. It has the characteristic property of imparting a red colour to turmeric, not unlike the tint produced by alkalies. This is best seen by dipping one half of a slip of turmeric paper in a solution of the acid (or of borax acidified with hydric chloride), and drying it at a gentle heat. The contrast between the dipped and the undipped portion will then be plainly seen.

821. It dissolves in alcohol, and the solution, when set fire to, burns with a beautiful green flame. This supplies an easy means of detecting the presence of boron in any body. In proof of this, a crystal of borax may be crushed to powder, and covered with hydric sulphate, which should be left to act upon it for a few seconds, so as to liberate the hydric borate. A little alcohol is then to be poured over the acidulated salt, and kindled, when the characteristic green flame will be seen.

822. Hydric borate appears to be a tribasic acid. A number of salts, called BORATES, may be derived from it; but the only important one is the sodic diborate, or borax, which occurs native, and may be obtained by adding sodic carbonate to hydric borate.



The crystallised salt contains 10 molecules of water of

crystallisation, and when heated, this water, as well as the elements of water from the salt itself, is given off, and finally a transparent glass-like residue of sodic metaborate (NaBO_2) is left.

823. Borax has a great tendency to form double salts with other radicles ; and hence it is used by tinmen and braziers in soldering, to act as a flux and to clean the surfaces which are to be joined, by dissolving the film of oxide which is formed at the high temperature necessary to melt the solder. It is also employed in the arts as a constituent of the finer varieties of glass, and in forming glazes for porcelain. It is used to a small extent in medicine.

824. Borax is also of much use to the analytical chemist, in consequence of its power of dissolving metallic oxides, which, in the majority of cases, form coloured glasses by combination with the salt. The tints of these compounds differ according to the metal present in them, so that their colours supply an accurate and easily applied method of identifying compounds before the blow-pipe. In illustration of this, the following experiments may be tried : (1.) A fragment of borax is to be placed in a small ring about 2 mm. in diameter formed at the end of a piece of thin platinum wire, and exposed to the blow-pipe flame till the water of crystallisation is expelled. A drop of solution of nitrate of cobalt is then to be let fall on the anhydrous salt, and this is to be treated a second time in the outer or oxidising flame of the blow-pipe, till it fuses into a clear globule. On allowing it to cool, it will be found to exhibit a deep blue colour which is characteristic of cobalt. (2.) If a similar experiment be made with manganic oxide, the globule or bead of borax will be of a violet colour. (3.) If a salt of the metal chromium be employed, the bead will be green. This method of testing will be alluded to in speaking of the different metals.

BORIC CHLORIDE.

| | Formula. | Weight. | |
|---------------|----------------|---------|----------------------------|
| Molecule..... | BCl_3 | 117.5 | 1 litre weighs 5.253 grms. |

COMPOSITION.

1 litre yields :

| | |
|--|----------------------|
| $1\frac{1}{2}$ litre of chlorine, | weighing 4.760 grms. |
| $\frac{1}{2}$ a litre of boron vapour (?), | " 0.493 " |

825. This is the only known compound of boron and chlorine. It is prepared by passing pure dry chlorine over amorphous boron gently heated in a glass tube. It is a very volatile liquid, boiling at 17° , fuming in the air, and decomposed by water into hydric borate and hydric chloride. Its chief interest consists in the fact that its composition, which has been accurately determined by Deville, is looked upon as deciding the atomic weight and atomicity of boron, since we know of no compound of boron and hydrogen, and are compelled to take its combination with chlorine, an equally well-defined monatomic element.

826. Boron also forms a compound with fluorine, the molecular formula of which is BF_3 . Boric fluoride is a colourless gas, decomposed by water in a manner analogous to the corresponding silicon compound (see par. 730, page 289).

Section VIII.—Tetratomic Element.

SILICON.

| | Symbol. | Weight. | |
|-----------|---------|---------|-----------------|
| Atom..... | Si | 28 | Density = 2.49. |

827. *Distribution.*—Silicon, like boron, does not exist in nature uncombined, but its oxide, silicic anhydride, or silica, as it is often termed, is the chief constituent of the crust of the globe. It forms, as it were, the stony skeleton of the earth. Thus sand, sandstone, and quartz are pure silica; granite and gneiss consist chiefly of silica; and a multitude of minerals, which by their aggregation form other rocks, such as trap,

basalt, lava, &c., are silicates—that is, compounds of various metals with a radicle containing silicon and oxygen. Silicon, indeed, is as abundant an element in the mineral world as the analogous carbon is in the vegetable kingdom.

828. Silicon may be obtained in several allotropic forms, closely analogous to those of carbon and boron.

(1.) *Amorphous Silicon*.—This may be obtained by heating potassic silicofluoride with about its own weight of potassium in a tube. It is a dull-brown powder, which may be fused at about the same temperature as steel, and burns brilliantly when heated in air.

(2.) *Graphitoidal Silicon*.—When amorphous silicon is intensely heated, it contracts in bulk, and becomes less easily oxidised. The best method, however, of obtaining silicon in this form is to fuse aluminium with potassic silicofluoride, and boil the mass with strong hydric chloride, when the silicon is left undissolved in the form of lustrous hexagonal scales. These may be heated to whiteness in oxygen without alteration.

(3.) *Diamond Silicon*.—This is procured by passing the vapour of silicic chloride over aluminium heated strongly in a porcelain tube. The chlorine unites with the aluminium, forming a volatile compound, while silicon is left behind in the form of brilliant octahedral crystals, which are hard enough to scratch glass.

Compounds of Silicon.

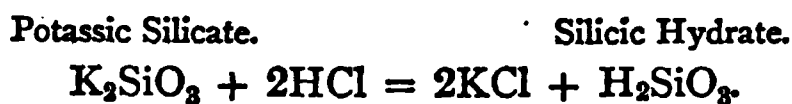
SILICIC ANHYDRIDE OR DIOXIDE.

| Formula. | Weight. | | Density of quartz = 2.64. |
|------------------------------|---------|--|---------------------------|
| Molecule..... SiO_2 | 60 | | |

829. This is the only known oxide of silicon. It occurs in a pure condition in quartz, or rock-crystal, which is often found beautifully crystallised in six-sided prisms with pyramidal ends, belonging to the hexagonal system. Chalcedony, agates, flints, white sand, and sandstones are all more or less pure forms of silica. It may be obtained in a pure amorphous condition by

the treatment of its less pure forms, or by the decomposition of silicates in the following way: The mineral containing it (such as felspar, granite, or sea-sand) is reduced to fine powder, and mingled with three or four times its weight of a mixture, in equal parts, of potassic and sodic carbonates. The whole is heated in a platinum crucible till it fuses into a glassy mass. The contents of the crucible are then boiled with water, to which hydric chloride in excess is afterwards added, and the whole evaporated to dryness. During the fusion, a mixture of potassic and sodic silicates is formed, while the other radicle of the original silicate is converted into a carbonate or oxide, carbonic dioxide being evolved in the latter case. On the addition of hydric chloride, the alkaline silicates are decomposed, a gelatinous precipitate of silicic hydrate is formed, and everything, except this, dissolves as chloride. The separated silicic hydrate is itself to some extent dissolved by the diluted acid, but after the evaporation of the liquid to perfect dryness, it loses its solubility, becoming silicic anhydride, and when acidulated water is poured upon the desiccated mass, it dissolves everything but the silica, which it leaves untouched.

830. This is an example of the usual way of decomposing and examining silicates. But some silicates—for instance, many of the clays, serpentine, and some felspars—are decomposed by strong hydric chloride or sulphate without previous fusion with alkaline carbonates. Another excellent method of decomposing silicates and obtaining pure silicic hydrate has been already described under the head of FLUORINE (page 289). The general nature of the reaction will be seen from the following equations:



The hydrate, when heated a little above 100° , gives off water:

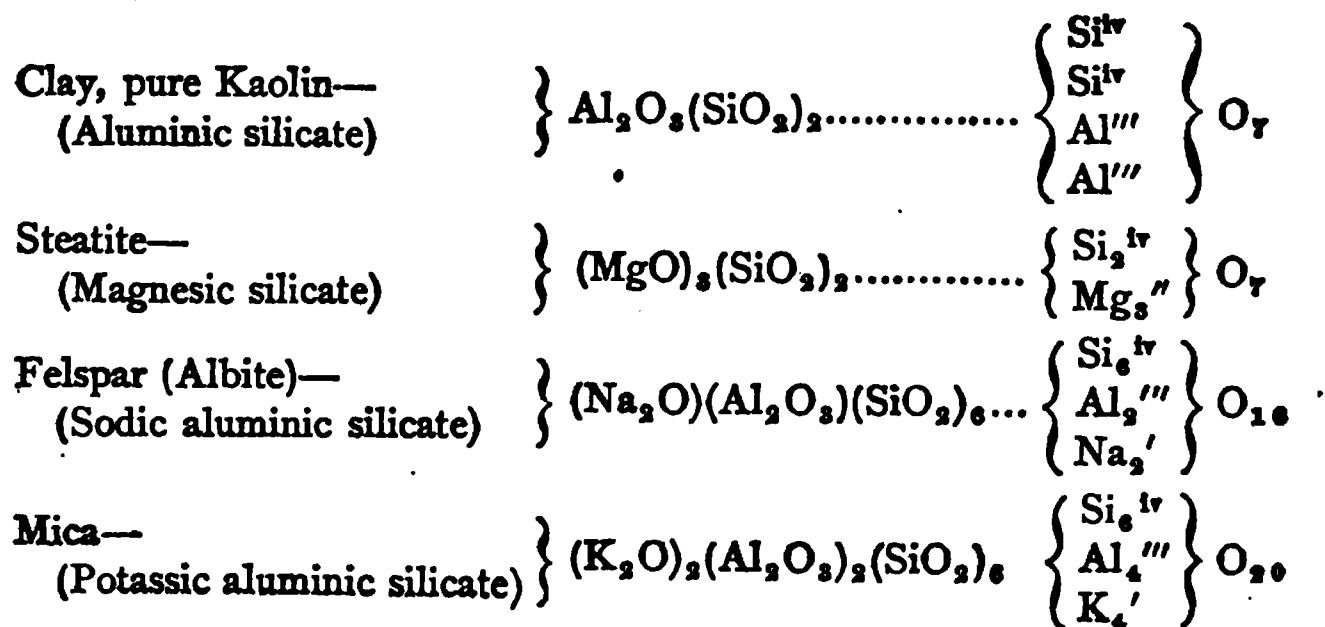


831. *Properties.*—Silica is a snow-white, gritty powder, which, after being strongly heated, is quite insoluble in water, acids,

and indeed most liquids. It is infusible by the most powerful wind-furnace, but melts when exposed to the intense flame of the oxyhydrogen blow-pipe. When it is heated in a globule of microcosmic salt (formed in a ring of platinum wire, like a borax bead, par. 824, page 330), before the ordinary blow-pipe flame, it floats in the globule unaltered and undissolved. Silicic anhydride dissolves easily in a boiling solution of potassic hydrate, forming potassic silicate, a member of a very large class of compounds which will be next described.

SILICATES.

832. These are substances which may be represented as containing a radicle consisting of silicon and oxygen, associated with various other radicles. A great variety of minerals are included under this head; and the constitution of silicates is very complex, owing to the high atomicity of silicon, which enables it to bind into one group several radicles, and thus form many different double salts. They may, of course, be regarded as direct combinations of metallic oxides with silicic anhydride; and they are often artificially formed in this way. But it would seem simpler to look upon them as formed by the replacement of hydrogen in a certain number of molecules of water, partly by silicon, partly by other radicles. The composition of a few silicates is given below.



833. *Silicic Hydrate*.—This substance, which ought more strictly to be called hydric silicate, is formed, as above noticed, by the action of hydric chloride or sulphate on a silicate, such as potassic silicate. It is a gelatinous mass, soluble to some extent in water. Many natural waters, such as those of the Geysers in Iceland, contain it in solution, and deposit it as they cool on the sides of the basin into which they flow. Chalcedony and the various agates and onyxes were probably formed in this way. A solution of pure hydric silicate may be obtained by Graham's method of 'dialysis,' which depends on the fact that crystalline substances (crystalloids) will pass through the pores of parchment, while non-crystalline substances (colloids, from *κίλλα*, glue) are retained. When, therefore, a liquid containing hydric silicate, such as is obtained by slowly adding a solution of potassic silicate to excess of hydric chloride, is placed in a vessel made by stretching parchment over a wooden hoop, and the vessel floated on water, the potassic chloride and excess of hydric chloride diffuse through the parchment, while a solution of hydric silicate remains behind. This solution, like that of carbonic dioxide, is feebly acid. It cannot be retained, as it soon solidifies into a transparent jelly.

834. *Glass*.—The various kinds of glass are mixtures of silicates, the value of which consists in their transparency, their fusibility, and the fact that they pass through a viscous condition before fusion, in which state they can be readily moulded into different shapes. We may distinguish two principal varieties of glass.

(1.) Flint glass, of which tumblers, decanters, white bottles, &c., are made. It is a mixture of potassic and plumbic (lead) silicates, and is made by fusing together pure white sand, red lead, and pearl-ash (potassic carbonate), in covered crucibles, set in a furnace. This glass is comparatively fusible, and, from its high refractive power, and its transparency and clearness, it is much used in making lenses and prisms. It is not, however, so unalterable as the other kinds: it is soft, and easily scratched, and liable to tarnish and change colour.

(2.) Crown-glass: this contains no lead, but is chiefly a mixture of calcic, sodic, and aluminic silicates. In its manufacture, sand, chalk, soda-ash (a crude sodic carbonate), and a variable quantity of broken glass, are mixed and heated until they just begin to agglomerate and form a pasty mass, called 'frit.' This is next transferred to large open crucibles, and raised to a higher temperature, until it is completely melted. A portion of aluminium is always taken up from the clay of the crucibles. This forms ordinary window-glass, and the coarser varieties are used for common wine bottles, &c., which owe their colour to the iron they contain. Plate-glass is essentially the same in composition; and when potassium is substituted for sodium, a very infusible glass is formed, of which the Bohemian tubing is made.

835. Various colours are imparted to glass by the admixture of certain metallic oxides during the fusion. Thus cobalt gives a deep blue glass, silver a yellow, chromium a green, and copper (when the suboxide is used) a ruby glass. Much of the coloured glass is only 'flashed,' or covered with a thin coating of coloured material by dipping the mass of white glass, before working it, into a pot of coloured glass. Patterns of different kinds may then be formed on the surface, by grinding away or dissolving (see under HYDRIC FLUORIDE) portions of the coloured stratum.

836. Glass is a very bad conductor of heat; and it is, in consequence, necessary to cool glass articles very slowly, to 'anneal' them, as it is called. As soon as they leave the hands of the workman, they are carried to a brick chamber, called the 'annealing oven,' which has been raised to a red heat. This is allowed to cool gradually, several days elapsing before it sinks to the temperature of the air. If this were not done, the surface of the mass would solidify before the interior, and thus the regular contraction of the cooling mass would be interfered with, the particles within being held in a state of constraint by the outer crust. A mere scratch, or a sudden change of temperature, will then be sufficient to cause a crack.

The 'Rupert's drops,' which are formed by dropping liquid glass into cold water, afford a striking illustration of the brittleness of unannealed glass. If the tail of one of these drops is broken off, the slight shock is sufficient to cause the whole drop to fly into powder. For a similar reason, glass flasks, retorts, &c., should always be carefully heated, a piece of wire-gauze, or a tray of sand, being, as a rule, interposed between them and the flame, in order to distribute the heat.

SILICIC CHLORIDE.

| | Formula. | Weight. | |
|---------------|-----------------|---------|---------------------------|
| Molecule..... | SiCl_4 | 170 | 1 litre weighs 7.59 grms. |

COMPOSITION.

1 litre yields :

2 litres of chlorine, weighing 6.346 grms.
 $\frac{1}{2}$ a litre of silicon vapour (?), " 1.244 "

837. This compound, which is chiefly of interest because it enables us to determine with probability the atomic weight of silicon, is prepared by passing dry chlorine over a mixture of silicic anhydride and charcoal, made into pellets and heated to redness in a porcelain tube. The reaction is :



It forms a colourless liquid, boiling at 59° , heavier than water, and quickly decomposed by the latter into hydric chloride and hydric silicate.

838. The compound of silicon with fluorine, silicic tetrafluoride, has been already described (page 288).

CHAPTER XVI.

THE METALLIC ELEMENTS.

Section I.—General Observations.

839. The metals are much more numerous than the non-metallic elements, forty-nine of the elements being usually reckoned to belong to the former class, while research holds out the expectation that more will be added to the number. Many of them, however, are rare, so that their properties cannot be made matter of general observation, and we shall discuss them, accordingly, more briefly than the other, the non-metallic class of simple substances.

840. The distinction between a metal and a non-metal is a purely artificial one. It is made chiefly for the sake of convenience, and is based upon physical rather than chemical criteria. It may, however, be broadly stated that a metal is distinguished from a non-metallic body by its possession of four characters, which are presented by it, as a rule, only when it is in mass, and not (or, at anyrate, in a much smaller degree) when it is in the state of a finely divided powder. These characters are the following:

(1.) It conducts heat excellently. This has been referred to already in the chapter on Heat. All metals are far superior in conducting power to any non-metallic body.

(2.) It is an equally good conductor of electricity. The employment of metals, such as copper, for lightning conductors, and in the construction of electric telegraphs, where they convey electricity almost instantaneously along several hundreds of miles of wire, sufficiently illustrates this character.

(3.) It reflects light powerfully. The peculiar brilliancy of burnished gold, silver, tin, &c., is an illustration of this character, which is distinguished as the *metallic* lustre. In consequence

of this, very little light is transmitted by metals—in other words, they are opaque, except in the thinnest films. Certain minerals, however, such as galena, specular iron ore, graphite, &c., possess an almost equally brilliant lustre.

(4.) It is an electropositive substance—that is, it is deposited at the negative pole of the battery (par. 250, page 94), when a solution of one of its compounds is submitted to electrolysis. This is an invariable rule. Every metal is electropositive, although it is true that several non-metallic substances are sometimes electropositive also.

841. On the whole, therefore, we may say that the possession of all these characteristics is necessary in order that a body may be considered a metal, although one or more of them may be found in a non-metallic body.

842. Although the above characters are shared by all metals, yet they possess them in very varying degrees. We shall proceed to give a general view of the properties of the metals, pointing out the limits of this variation.

843. (1.) *Weight.*—The majority of the useful metals are between seven and eight times heavier than an equal bulk of water. A few, such as potassium, are lighter than water. One, platinum, is twenty-one times heavier. Lead, which is eleven times heavier than water, stands midway between the two extremes.

TABLE OF DENSITIES.

(Water at 0° C. = 1.000.)

| | | | |
|----------------|-------|---------------|------|
| Lithium..... | 0.593 | Cobalt..... | 8.5 |
| Potassium..... | 0.865 | Cadmium..... | 8.7 |
| Sodium..... | 0.972 | Nickel..... | 8.8 |
| Rubidium..... | 1.52 | Copper..... | 8.9 |
| Magnesium..... | 1.75 | Bismuth..... | 9.8 |
| Aluminium..... | 2.56 | Silver..... | 10.5 |
| Arsenic..... | 5.96 | Lead..... | 11.3 |
| Antimony..... | 6.70 | Thallium..... | 11.9 |
| Zinc..... | 7.1 | Mercury..... | 13.6 |
| Tin..... | 7.3 | Gold..... | 19.3 |
| Iron..... | 7.8 | Platinum..... | 21.5 |
| Manganese..... | 8.0 | | |

844. (2.) *Condition*.—Nearly all the metals are solid at ordinary temperatures. One is a liquid, namely, mercury; and as there is every reason to believe that, if we could condense hydrogen, we should find it possessing all the metallic characters, we may say that one is a gas. They change their state, moreover, at very various temperatures. Platinum is scarcely fusible at the highest temperature of a furnace; iron melts at a rather lower point; silver melts at a lower point still, a bright red heat; while potassium melts below the boiling-point of water, and may be converted into vapour at a red heat; and the melting-point of mercury (commonly called its freezing-point) is 39° below zero. Certain of the metals, such as potassium, sodium, iron, and platinum, become pasty and adhesive (pass through, in fact, a viscous state) at temperatures much below their melting-points. In virtue of this property, the first two metals can be moulded like wax at 16° ; pieces of iron are welded, that is, compressed into one, at a bright red heat, and particles of platinum at a white heat.

TABLE OF MELTING-POINTS.

| | | | |
|----------------|----------------|-----------------------|----------------|
| Mercury..... | $- 39^{\circ}$ | Antimony..... | 432° |
| Potassium..... | $+ 58^{\circ}$ | Silver..... | 1000° |
| Sodium..... | 90° | Copper..... | 1090° |
| Tin..... | 230° | Gold..... | 1250° |
| Bismuth..... | 256° | Cast-iron..... | 1300° |
| Cadmium..... | 321° | Wrought-iron..... | 1650° |
| Lead..... | 334° | Platinum (about)..... | 2000° |
| Zinc..... | 360° | | |

845. The metals which are solid at ordinary temperatures all readily assume regular geometrical forms—that is, occur in crystals; and the majority of them exhibit crystalline shapes which belong to the same system—namely, the *regular* system (par. 74, page 36). The most common of these are the cube and the regular octahedron. Arsenic, tellurium, and antimony do not crystallise in cubes and octahedrons, but in another shape, called the rhombohedron, which has six faces, like the cube, but differs from it in its faces not being squares, but

rhombic or diamond-shaped, and in its angles not being right angles.

846. (3.) *Cohesion*.—A very great difference is observed among the metals in what is called *malleability*—that is, in their susceptibility of being beaten out or rolled into sheets or leaves. The highly crystalline metals—such as antimony, bismuth, and, at ordinary temperatures, zinc—are brittle, and break into fragments when struck with the hammer or passed between rollers. The less crystalline metals, especially those which unite softness with tenacity, exhibit malleability in the highest degree, so that, like gold, they may be beaten into leaves which are only $\frac{1}{10,000}$ th of a millimetre in thickness. These malleable metals admit also, in general, of being drawn out into wires of great fineness, and are then said to exhibit ductility. Gold is as ductile as it is malleable, but it is otherwise with several of the malleable metals. Iron and platinum are, both of them, highly ductile; the latter has been obtained, in the form of wire, not more than $\frac{1}{1200}$ th of a millimetre in diameter. Neither platinum nor iron, however, admits of being beaten out into very thin leaves. The order of tenacity, which is measured by the weight which the metal, drawn into wire of a given thickness, can sustain, is different, iron being at the head of the list.

TABLE SHEWING THE ORDER OF

| MALLEABILITY. | DUCTILITY. | TENACITY. |
|---------------|------------|-----------|
| Gold. | Platinum. | Iron. |
| Silver. | Silver. | Copper. |
| Copper. | Iron. | Platinum. |
| Tin. | Copper. | Silver. |
| Lead. | Gold. | Zinc. |
| Zinc. | Aluminium. | Gold. |
| Platinum. | Zinc. | Tin. |
| Iron. | Tin. | Lead. |
| | Lead. | |

847. (4.) *Chemical Affinities*.—The most general chemical character of the metals is their basic property—that is, their

readiness to combine with electronegative bodies, such as oxygen, with the evolution of light and heat, or at least of heat. The majority of the metals burn readily in air, or, failing that, in pure oxygen, as may be seen by heating tin, zinc, antimony, &c., before the common, or, still better, the oxyhydrogen blow-pipe, or by exposing them in crucibles to the heat of a furnace or smith's forge. Iron, also, as has been mentioned under oxygen, burns brilliantly in that gas. The rarest and most precious of the metals, as silver, gold, and platinum, are not combustible, but, on the other hand, have their affinity for oxygen lessened by raising their temperature.

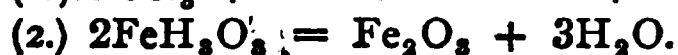
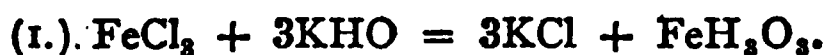
848. All the metals, without exception, combine with sulphur, generally in more than one proportion. The same remark applies to chlorine, bromine, iodine, fluorine, and to the other electronegative radicles.

849. To avoid repetition under the head of the individual metals, we state here some general facts concerning the mode in which the chief metallic compounds are obtained :

850. *Oxides*.—(1.) Many oxides, such as ferric oxide (hematite) and manganic oxide (pyrolusite), occur native, and in a state of purity.

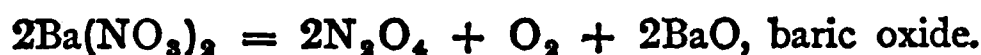
(2.) Others are readily procured, by the combustion of the metals in air, or oxygen, or by heating the metal with a substance, such as potassic nitrate or chlorate, capable of affording oxygen.

(3.) A third and very frequent method is to heat the hydrate which is procured by the addition of an alkali, such as potassic or sodic hydrate, to a solution of a salt of the metal. Thus, to procure ferric oxide, we add a solution of potassic hydrate to a solution of ferric chloride, and heat nearly to redness the precipitated ferric hydrate.



In some cases, as with silver, the oxide, not the hydrate, is at once precipitated from solutions.

(4.) A fourth method of procuring metallic oxides is by heating a salt formed by the metal with a volatile acid containing oxygen. Thus, mercuric oxide, cupric oxide, and baric oxide are obtained by heating their respective nitrates :



851. The three general classes into which oxides may be divided have been already mentioned (page 174). It sometimes happens that a metal forms oxides which, according to the proportion of oxygen they contain, are basic, neutral, or acid ; the lowest oxide being generally the most strongly basic. The oxides of manganese supply the best illustration of this, as the following table will shew :

| | |
|--|---|
| (Permanganic Anhydride, Mn_2O_7)..... | Not isolated, forms with water an acid. |
| (Manganic Anhydride, MnO_3)..... | " |
| Manganic Dioxide, MnO_2 | Neutral. |
| Manganic Sesquioxide, Mn_2O_3 | Feebly basic. |
| Manganous Oxide, MnO | Strongly basic. |

The higher oxides, including all those which are not basic, generally shew a tendency to give off some of their oxygen.

852. *Sulphides*.—(1.) Many metallic sulphides are found native, as already more than once mentioned.

(2.) The immense majority of the metals unite readily with sulphur when heated with it. In this way various sulphides, such as ferrous sulphide, referred to under HYDRIC SULPHIDE, are prepared.

(3.) Hydric sulphide, or any other soluble sulphide, when brought in contact with a solution of a metallic salt, generally causes the formation of a sulphydrate, or of a sulphide.

(4.) A few sulphides scarcely to be prepared in any other way, are procured by heating the corresponding sulphate with charcoal, which removes the whole of the oxygen, leaving the sulphur in combination with the metal. Thus, baric sulphate, when heated with charcoal, forms baric sulphide and carbonic dioxide :



853. The combinations of the metals with other radicles may be effected in one or other of the ways above indicated. Thus, to sum up, their salts may be obtained :

(1.) By the direct combination of the metal with a radicle. For instance, ferric chloride by the union of iron with chlorine :



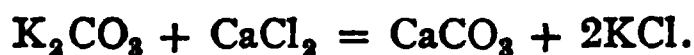
(2.) By the combination of an oxide with an anhydride. Calcic oxide with sulphuric anhydride forms calcic sulphate :



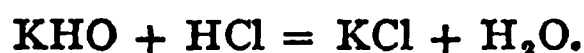
(3.) By the substitution of a metal for hydrogen in an acid. When zinc is acted on by hydric sulphate, hydrogen is evolved, and zinc sulphate formed :



(4.) By double decomposition between two salts. Thus, when potassic carbonate is added to a solution of calcic chloride, calcic carbonate is precipitated, while potassic chloride remains in solution :



When potassic hydrate is added to hydric chloride, potassic chloride and water are formed :



A carbonate is often substituted for the hydrate or oxide in the process last described. In this case, carbonic dioxide is given off with effervescence, and the ultimate product is the same as if the oxide had been taken.

854. The proportions in which a metal combines with oxygen generally bear a simple relation to those in which it combines with other radicles ; so that, if the formulæ of the oxides of a metal are known, those of its sulphides, chlorides, sulphates, &c. may to a great extent be predicted.

855. Many of the metals combine with each other to form peculiar compounds called 'alloys,' in which the general

appearance of a metal is preserved, while the fusibility, malleability, &c. of the compound often differ widely from those of its constituents. These alloys are not often obtained in such a definite form as other salts, since they dissolve readily in excess of the melted metals, and cannot, as a rule, be separated by crystallisation. Such mixtures, or solutions of the alloys, are, from the modified properties which they often exhibit, of great practical use. A sufficient illustration of their value is afforded by the alloys formed by melting together copper and tin. Copper is not hard enough, and tin is not tenacious enough for many purposes; but by alloying it with increasing proportions of tin, we obtain: (1.) Gun metal, an extremely tenacious, moderately hard, but not brittle alloy; (2.) Bell metal, which is harder, but still tough; (3.) Speculum metal, a very hard brittle substance, which is susceptible of a high polish. The uses of these alloys are sufficiently indicated by their names. There is one remarkable alloy called 'fusible metal,' composed of tin, lead, and bismuth. None of the metals which compose it melt under 230° , but the alloy itself melts below the boiling-point of water. The alloys of mercury with other metals are called 'amalgams,' an old alchemical name.

856. *Occurrence and Distribution of the Metals.*—Some of the metals, such as gold, occur in nature in small quantity. Others, like iron, are very abundant. A few—such as the metals gold and platinum—occur either uncombined, or associated only with other metals. The great majority, however, are found solely in combination, partly with other metals, but chiefly with non-metallic elements, such as oxygen and sulphur. These native compounds are called the ores of the metals. This term, which is a metallurgical rather than a chemical one, is applied to any native metallic compound which is smelted or otherwise wrought, so as to procure from it the metal it contains. Ores are occasionally alloys, or combinations of different metals; such, for example, are the ores of platinum, in which that metal is associated with palladium, rhodium, iridium, and osmium.

More frequently ores are salts, or oxides of the metals. Thus two of the most valuable ores of iron are oxides, and a third is the carbonate. The most abundant ores of lead, zinc, copper, and antimony are sulphides. Carbonates are pretty frequent; sulphates are less so: but any native metallic compound is an ore which occurs in sufficient quantity to make it worth the metallurgist's while to extract metal from it.

857. Occasionally these metallic ores find a place among the regular strata or layers which compose the more recently deposited portions of the earth's crust. For instance, the iron ore called clay iron-stone is found in thin bands between the beds of coal in Staffordshire and South Wales. When this is the case, the ore has most probably been deposited from solution. But far more generally, the ores occur among the older non-stratified rocks, which bear marks of volcanic origin, such as granite, quartz rock, and basalt. They often fill up fissures which extend upwards through the more recent strata, and constitute what are called by mineralogists veins or lodes.

858. We have abundant evidence that many of the metals present in the earth exist elsewhere in space. Besides the fact that meteorites, which seem to be fragments of some shattered planet, are largely composed of iron, nickel, and other metals, the results of spectrum analysis (pages 80, 81) have shewn that the sun and stars contain many metals in the state of vapour.

CLASSIFICATION OF THE METALS.

859. Many different modes of classifying the metals have been proposed, according to the point of view from which they are regarded. The physicist would arrange them in groups according to their densities, or their relations to heat, light, &c. The mineralogist would classify them according to their occurrence in the earth, as alkaline metals, earthy metals, precious or noble metals, and so on. The chemist would divide them according to their affinities and the character and composition of the compounds they form. Thus, some metals

have so great an affinity for oxygen that they decompose water at ordinary temperatures, such as potassium and calcium; others only decompose water at a red heat, such as iron and copper; others do not decompose it at all, such as gold and platinum.

860. But the most scientific basis of classification appears to be the atomicity of the substance. This has already served to classify the non-metallic elements, and it is extremely desirable to extend it also to the metals. We are met at the outset by the difficulty, that very few of the metals form, with hydrogen, compounds which can be isolated and examined; and we must therefore have recourse to some other element as our standard of atomicity. Such an element is chlorine; it is as well defined a monatomic element as hydrogen, and it forms compounds with all the metals. With many of them, however, it forms more than one compound; and the question arises, which of these compounds are we to take as defining the true atomicity of the metal? Tin, for instance, forms two chlorides—stannous chloride (SnCl_2), and stannic chloride (SnCl_4): is the metal to be placed in the diatomic or the tetratomic class? No conclusive answer can be given in the present state of our knowledge; but it seems most rational to consider that compound which contains most chlorine as indicating the true atomicity of the substance, uncomplicated by any theories of partial self-saturation (par. 420, page 160), which may, if thought necessary, be brought in to account for the existence of the lower compounds.

861. The large groups thus formed may then be divided into smaller groups, or families, composed of elements which closely resemble each other in chemical and physical properties.

TABLE OF THE PRINCIPAL METALS.

| MONATOMIC. Typical Chloride, K'Cl. | DIATOMIC. Typical Chloride, Ba''Cl ₂ . | TRIATOMIC. Typical Chloride, Al'''Cl ₃ . | TETRATOMIC. Typical Chloride, Sn ^{iv} Cl ₄ . | PENTATOMIC.* Typical Chloride, Sb ^v Cl ₅ . |
|---|--|---|---|--|
| Potassium. Rubidium. Cæsium. Sodium. Ammonium. —— Lithium. —— Silver. | Barium. Strontium. Calcium. —— Magnesium. Zinc. Cadmium. —— Copper. Mercury. Lead. | Aluminium. Chromium. —— Iron. Cobalt. Nickel. Manganese. —— Uranium. —— Vanadium. —— Gold. —— Thallium. —— Molybdenum. Tungsten. | Tin. Titanium. —— Platinum. Palladium. Iridium. Osmium. Rhodium. Ruthenium. | Antimony. Arsenic. —— Bismuth. * See page 471. |

862. Another mode of classification which is practically a convenient one, depends upon the methods employed for the separation of the different metals in the course of an analysis. If a solution containing salts of all the metals is taken, and hydric chloride added to it, silver, mercury (monatomic), and most of the lead, are separated as insoluble chlorides. If to this acid solution some hydric sulphide is added, a large group of metals, such as copper, tin, gold, &c., are separated as sulphides. If the clear solution is now neutralised, and some ammoniac sulphide added, other metals, such as iron, zinc, &c., are separated, since they form sulphides which, though soluble in acids, are insoluble in water. Again, if the remaining liquid is mixed with ammoniac carbonate, barium, strontium, and calcium are precipitated as carbonates. Magnesium may next be separated by ammoniac phosphate, and we have then

in solution only the alkali metals, which form a group by themselves. It is thought worth while to insert a table shewing this analytical classification, since many may find it convenient to study the metals in the order suggested by their work in the laboratory.

TABLE SHEWING THE DISTRIBUTION OF THE MORE IMPORTANT METALS INTO GROUPS FOR THE PURPOSES OF ANALYSIS.

| | |
|---|--|
| <p>I.</p> <p>Metals which are separated from solutions by Hydric Chloride.</p> <p>Silver. Mercury (monatomic). Lead (partially).</p> | <p>III.</p> <p>Metals which are separated from solutions by Ammonic Sulphide.</p> <p>Zinc. Manganese. Nickel. Cobalt. Iron. Chromium. Aluminium.</p> |
| <p>II.</p> <p>Metals which are separated from solutions containing hydric chloride by Hydric Sulphide.</p> <p>Lead. Mercury (diatomic). Bismuth. Copper. Cadmium. Arsenic. Antimony. Tin. Gold. Platinum.</p> | <p>IV.</p> <p>Metals which are separated from solutions by Ammonic Carbonate.</p> <p>Barium. Strontium. Calcium.</p> <p>V.</p> <p>Metal which is separated from solutions by Ammonic Phosphate.</p> <p>Magnesium.</p> <p>VI.</p> <p>Metals which are not separated from solutions by the above reagents.</p> <p>Potassium. Sodium. Ammonium.</p> |

Section II.—Monatomic Metals.

POTASSIUM.

| | Symbol. | Weight. | |
|-----------|---------|---------|------------------|
| Atom..... | K | 39 | Density = 0.865. |

863. Potassium occurs in nature abundantly, but solely in combination. It is found primarily in granite, trap, and other igneous rocks, associated with different bases in the condition of silicates. From these rocks, as they crumble down, it finds its way into soils, which are uniformly barren if devoid of potass. Growing plants extract it from the soil; and when they are burned it forms a chief ingredient of their ashes. It occurs in small quantity also in animals, in natural waters, and in the sea. The metal was discovered in 1807 by Sir Humphry Davy, and was one of the earliest results of the employment of a powerful galvanic battery which he had caused to be constructed for the Royal Institution. He obtained it by passing the electric current through a moistened piece of potassic hydrate, which had been, up to that time, considered to be a simple substance. Oxygen was evolved at the positive pole, while bright shining metallic globules appeared at the negative pole, and quickly burned away with a violet light.

864. *Preparation.*—Potassium is now usually prepared in the following way. Hydric potassic tartrate (cream of tartar) is ignited in a covered crucible, and the residue, consisting of carbon and potassic carbonate, is heated to whiteness in an iron retort, when the following reaction takes place :



The metal distils over and is condensed in shallow iron receivers filled with naphtha. The process is a dangerous one, not only from the inflammability of the metal, but also because an explosive compound is formed, probably a combination of potassium with carbonic oxide, from which the metal must be freed by a second distillation. For these reasons, the metal is

somewhat costly; but very small fragments will suffice for the performance of many striking experiments.

865. Potassium has a brilliant white colour with a shade of blue. At the ordinary temperature of the air it is soft like wax, so that it can be readily cut by a knife, or moulded with the fingers. At 0° , it is brittle and crystalline; at 25° , semi-fluid; at 62.5° , completely liquid, and it may be distilled at a low red heat, forming a vapour of a green colour. It is considerably lighter than water, its density being 0.865, compared with water 1.000.

866. The lustre of potassium disappears instantaneously if it be exposed to the air, owing to its combination with oxygen and conversion into the white potassic oxide. Hence it must be kept under the surface of naphtha, a substance which contains no oxygen and has no action upon it.

867. The following experiments may be tried with the metal:

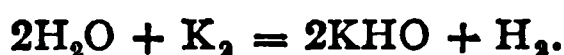
(1.) If a fragment be heated in a small iron spoon till it begins to rise in vapour, it takes fire, burning with a violet flame.

(2.) If a fragment be thrown on the surface of water, it floats (being lighter than water), and kindles spontaneously, burning with a beautiful purple flame, and combining with the oxygen and some of the hydrogen of the water, as mentioned under HYDROGEN.

(3.) If this experiment be made with water coloured by cabbage infusion, the latter will change to green as the potassium burns.

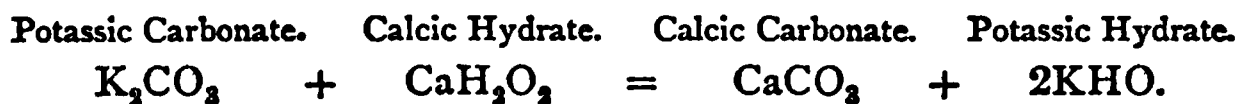
(4.) If a piece of potassium be laid upon ice, it will take fire as if upon water, melting a hole in it with great rapidity.

868. The substance formed in the above experiments is potassic hydrate, one of the atoms of hydrogen in the molecule of water being replaced by an atom of potassium, thus:



It is the substance commonly known under the name of 'caustic potash,' and is of considerable importance. It is

prepared on the large scale by adding slaked lime (calcic hydrate) to a boiling dilute solution of potassic carbonate :



The calcic carbonate and excess of calcic hydrate are allowed to subside, and the liquid is then poured off and evaporated down in a loosely covered silver basin, the heat being finally raised nearly to redness, when the melted potassic hydrate is poured into cylindrical iron moulds, in which it consolidates. It is sold in the shops, accordingly, in the form of sticks, and must be preserved in stoppered bottles, otherwise it absorbs moisture with great rapidity, and runs into a liquid. It is often employed to withdraw carbonic dioxide and other gases from gaseous mixtures.

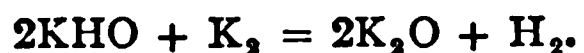
869. Solution of potassic hydrate is intensely acrid to the taste, and highly caustic, so that it should be tasted only when much diluted. It exhibits the characteristic properties of an alkali in the highest degree. These, it will be remembered, are—1. A peculiar taste; 2. The power of converting certain vegetable reds into blues or greens, and vegetable yellows into browns; 3. The power of neutralising or destroying the characteristic properties of acids when added in sufficient quantity to them. The student may observe all these properties with solution of potash.

870. The further experiment may be tried of exposing some of the potash solution in a shallow vessel to the air, when it will be found after a time to become milder in taste, and to effervesce when mixed with an acid, owing to its having absorbed carbonic dioxide from the air. To prevent this absorption occurring, solutions of potash should be preserved in stoppered bottles.

871. If the solution of potash be shaken in a bottle with olive or any of the other fixed oils, a viscid semi-transparent solution will be formed, containing ordinary soap. The experiment will illustrate an important use of the alkalies—namely, in the soap manufacture. The various soaps are salts of

potassium or sodium in combination with organic acid radicles, chiefly oleate and stearate, which are present in oils and fats. Potassic oleate is the chief constituent of the 'soft soaps,' which are made by boiling down a mixture of tallow, or linseed oil, with a solution of potassic hydrate ('potash-lye'), until it solidifies on cooling.

872. *Potassic Oxides*.—There appear to be three compounds of potassium and oxygen, represented by the formulæ K_2O , K_2O_2 , and K_2O_4 . When potassic hydrate is heated with the proper proportion of potassium, the metal replaces the atom of hydrogen, and potassic oxide is formed :



When potassium is moderately heated, first in a current of dry air, and then in a current of oxygen gas, a yellow powder consisting of potassic tetroxide is eventually obtained. This is rapidly decomposed by water, oxygen being given off, and a solution of potassic di-hydrate (KH_2O_2) being formed.

873. *Potassic Carbonate* (K_2CO_3).—This is the source of many other potassic salts. It is known in its crude form by the name of pot-ashes or pearl-ashes, and is prepared in large quantities in America and Russia, where wood is abundant. The ashes of the burned wood are lixiviated—that is, placed in large barrels, which are then filled up with water. After some time, the water is drawn off from below, saturated with soluble matter, and when boiled down to dryness in large iron caldrons, forms the crude pot-ashes, and, when further purified, the pearl-ashes of commerce. Both are very impure, from the presence of potassic silicate, sulphate, chloride, &c. The pure carbonate is obtained by calcining cream of tartar, digesting the calcined mass in water, and evaporating the filtered liquid to dryness.

874. Potassic carbonate has an alkaline taste and action upon colouring matter. It also possesses causticity, but these characters are less strongly marked than in potassic hydrate. The carbonate is an important salt, being used in medicine, in

the manufacture of soft soap, and of glass, as well as in other arts. It is also consumed in the laboratory in the preparation of potassic hydrate.

875. *Potassic Nitrate, Nitre, or Saltpetre* (KNO_3).—This valuable salt is brought to this country chiefly from the East Indies, where, as in other warm climates, its formation is constantly going on in the soil. It is also made artificially in large quantities by heaping together animal and vegetable refuse containing nitrogen, together with wood-ashes and lime, sprinkling the heaps with water, and leaving them exposed to the air for some time. Potassic nitrate is formed during the putrefaction, and is washed out by water, and crystallised. Its employment as a source of hydric nitrate has been referred to under that substance. It is consumed also to a considerable extent as an antiseptic.

876. Its other great use is as a constituent of gunpowder, of which it forms the chief part by weight, the other ingredients being charcoal and sulphur. These substances are mixed very nearly in the proportion of two equivalents of nitre, one of sulphur, and three of carbon, or 75 parts by weight of nitre, 15 of carbon, and 10 of sulphur. The ingredients, after being mixed, are made into a paste with water, and ground for some hours between stones. The mass is then compressed into cakes, which are afterwards broken up, or granulated between rollers. The rapidity of inflammation of gunpowder depends in a great measure on the size of these grains, and they are carefully selected for the different purposes. Thus the smallest-grained powder is used for rifles, while the 'pebble-powder,' now used for the largest guns, consists of pellets larger than almonds. Such a powder ignites slowly, and the shot is subjected to a gradually increasing pressure as it travels along the bore of the gun: the strain on the latter, moreover, is much lessened. When gunpowder is kindled, the oxygen of the nitre combines with the carbon, forming carbonic oxide, or carbonic dioxide, whilst the sulphur unites with the potassium of the nitre, and the nitrogen is set free. The amount of gas

thus produced occupies a space 400 times greater at the ordinary temperature than the gunpowder which evolves it does before being fired. But the heat produced by the combustion triples at least the volume of the gases. It is this rapid expansion of gunpowder to a bulk some 1500 times greater than it possessed before being kindled, which confers on it its great propulsive and disruptive powers. The decomposition of gunpowder may be represented approximately by the following equation :



877. *Potassic Sulphates*.—The neutral sulphate (K_2SO_4), and the 'bisulphate,' or potassic hydric sulphate (KHSO_4), are both obtained in the manufacture of hydric nitrate, as already explained (par. 536, page 209). They are used in the manufacture of alum, in calico printing, and to a certain extent in medicine.

878. *Potassic Chlorate* (KClO_3).—The preparation of this salt, and its importance as a source of oxygen, have been already mentioned (page 272).

879. *Potassic Sulphides*.—The protosulphide (K_2S) is obtained by heating potassic sulphate with charcoal. It forms a crystalline mass, soluble in water, and possessing a caustic, bitter, sulphureous taste. By fusing this compound with sulphur, a bisulphide, K_2S_2 , and a tersulphide, K_2S_3 , may be obtained. A pentasulphide, K_2S_5 , is also known.

880. *Potassic Chloride* (KCl) is procured in the process for potassic chlorate, as mentioned under CHLORIC ACID. It is also left as the residue when potassic chlorate is heated till it parts with all its oxygen, as stated under that gas. It is likewise one of the constituents of kelp, referred to under IODINE, and is extensively extracted therefrom. It closely resembles common salt in appearance, and is employed in the manufacture of the important substance alum, and in the conversion of sodic nitrate into potassic nitrate.

881. *Potassic Iodide* (KI) is of more interest as a preparation

of iodine than as a salt of potassium. Its properties as an iodine compound have been discussed under HYDRIC IODIDE.



Fig. 74

882. *Tests for Potassium.*—A salt of potassium—that is, such a body as potassic chloride or nitrate—is distinguished from all bodies, but compounds of the other metals of the same group, by the two following characters, which the student can observe, with a solution of any pure salt of potassium, such as the nitrate. To one portion of the solution contained in a wine-glass or test-tube (fig. 74), solution of ammoniac sulphide is added, which will occasion no precipitate, because potassic sulphide is soluble. To another portion in a second glass, solution of ammonia, and then a drop or two of solution of sodic phosphate, are added—no precipitate will be formed.

883. These negative results prove that either potassium, sodium, or ammonium is present, but the choice is limited to one of these three (lithium, owing to its rarity, being excluded from consideration), for the salts of all the other metals cause a precipitate on addition of one or both of these reagents.

884. That it is potassium which is the metal present, is ascertained by the following tests :

(1.) To one portion of the solution, tartaric acid (hydric tartrate) dissolved in water is added. It will produce a white crystalline precipitate, consisting of potassic hydric tartrate (cream of tartar).

(2.) To a second portion of the solution of the salt of potassium, solution of platinic tetrachloride is added. It will produce a yellow crystalline precipitate of potassic platinic chloride (KPtCl_5).

(3.) A third portion of the original solution is evaporated to dryness, or, to save this trouble, a portion of the dry salt with which the solution was made is taken and moistened with alcohol, which is then set fire to. It will burn with a faint violet flame, such as potassium itself exhibits when kindled.

The same phenomenon will take place if the potassium salt laid upon charcoal, or held in a loop of platinum wire, be heated in the inner or reducing flame of the blow-pipe. The violet flame is in both cases indistinct if much sodium is present. If, however, a piece of blue glass is held in front of the eye, the yellow rays are absorbed, while the violet rays pass through unchanged. In this way a very small trace of potassium may be recognised.

885. When the violet light, due to incandescent potassium vapour, is examined in a spectroscope, it is found to contain rays of very various refrangibilities. A nearly continuous spectrum is observed, with one bright line near the red end, corresponding with the line A in the solar spectrum, and another line in the violet, also corresponding with a solar line. Hence it is inferred that potassium exists in the sun (see the chapter on LIGHT).

886. We have gone over the tests for potassium in combination more fully than we shall discuss those of most of the subsequent metals, as it is the first under notice. The beginner should be exercised in the application of the tests by having a salt given him of one of the alkalies, with instructions to ascertain whether it be a compound of potassium or not; and so also with the other metals.

SODIUM.

| | | | |
|-----------|---------|---------|------------------|
| | Symbol. | Weight. | |
| Atom..... | Na | 23 | Density = 0.972. |

887. *Distribution.*—Sodium occurs in nature abundantly in combination, but nowhere free. Its most important native compound is its chloride, which, as rock-salt, occurs in immense beds in the solid crust of the earth, and in solution in probably every natural spring-water, as well as in the sea. Compounds of sodium occur in many minerals, and in most soils. They are found in small quantity in the majority of land plants, but largely, as kelp illustrates, in those of the sea. Sodium

also occurs abundantly as common salt in the structures of the higher animals.

888. *Preparation.*—Sodium is prepared on the large scale from a mixture of dry sodic carbonate, 30 kilogrms., powdered charcoal, 13 kilogrms., and finely powdered chalk, 3 kilogrms. The whole is kneaded into an intimate mixture or paste with oil, and distilled in an iron retort, when the metal sodium passes over in vapour, and is received in naphtha. It is more easily and safely obtained than the metal potassium, and is consequently much cheaper. It has lately been manufactured in large quantities, to be employed in the reduction of aluminium and magnesium.

889. *Properties.*—Sodium has a bright lustre and a white colour, with a shade of red. It is soft, and readily moulded at 15° , melts at 97° , and rises in vapour at a red heat. It is lighter than water, its specific gravity being 0.972.

890. The following experiments may be tried with it:

(1.) Thin slices exposed to the air will be found to tarnish and grow dim rapidly; and, finally, to become converted into a soft, white substance, which is sodic oxide (Na_2O), or 'soda.'

(2.) A fragment heated in a spoon burns with a yellow flame.

(3.) An irregular fragment thrown upon the surface of cold water will rapidly assume a globular form, and roll along the surface with great rapidity, decomposing the water as potassium does, but, unlike it, not catching fire.

(4.) If this experiment be repeated with hot water, or if the sodium be laid on a piece of metal, and a drop or two of water allowed to fall on it, it will kindle, and burn with its rich yellow colour. If infusion of purple cabbage be substituted for pure water, it will be coloured green by the soda produced.

891. The substance here formed is sodic hydrate (NaHO), as in the case of potassium. This substance is obtained in solution by boiling lime with sodic carbonate dissolved in water. When the liquid thus procured is evaporated to dryness, it leaves a solid residue of the hydrate, which is fusible, highly

soluble in water, caustic, powerfully alkaline, and closely analogous to potassic hydrate in all its properties.

892. *Sodic Oxides*.—The monoxide (Na_2O) may be obtained by heating sodic hydrate with sodium, the reaction being similar to that described under POTASSIUM. When sodium is heated in a current of oxygen, a dioxide (NaO_2) is obtained in the form of a white powder, which dissolves readily in water without giving off oxygen.

893. *Sodic Nitrate* (NaNO_3) occurs abundantly in Peru, where it is found covering the soil in many districts. It deliquesces in damp air, and burns much more slowly with combustibles than potassic nitrate. These properties make it unsuitable for the manufacture of gunpowder; but it is largely consumed as a source of hydric nitrate, and is employed in agriculture.

894. *Sodic Sulphate* ($\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$).—This salt, which was formerly called Glauber's salt, is manufactured in large quantities by the action of hydric sulphate on sodic chloride, and is the residue of the process for hydric chloride, as mentioned under that substance. It is used to some extent in medicine, but is chiefly manufactured with a view to its conversion into sodic carbonate. An experiment is given at page 65.

895. *Sodic Chloride*, or 'common salt' (NaCl).—This has been already mentioned as the principal source both of sodium and chlorine. It occurs both in sea-water and in extensive beds beneath the marls of the triassic system in Cheshire; and also in Poland and Spain. It is known as 'rock-salt,' or 'sal gem,' which is nearly pure sodic chloride, often coloured red by iron, but sometimes found in large colourless transparent crystalline masses, which are valuable in experiments on radiant heat, from the large amount of heat-rays which pass through unabsorbed.

896. Most of the common salt of commerce is obtained by the evaporation of sea-water, or the water of brine-springs which has taken it up from the beds of rock-salt through which it passes. The sea-water is let into large shallow basins, and evaporated by exposure to the sun and air. The sodic chloride,

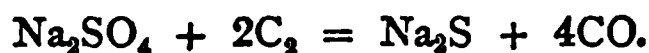
being the least soluble of the salts present, crystallises out first, leaving the magnesian chloride, &c. in solution. In Germany and Poland, the water from the brine-springs, or from the salt-mines, is pumped up to some height, and then allowed to trickle down loosely-piled fagots or ropes, on which it crystallises; the liquor which drains off being further concentrated in pans. Sodium chloride, like the other chlorides, iodides, &c. of this group, crystallises in well-defined cubes; but in the manufacture of table-salt the evaporation is carried very far, with constant stirring, so as to obtain the salt as a fine crystalline powder.

897. *Sodic Carbonate* ($\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$) is one of the most important chemical substances, from its consumption in bleaching, glass-making, soap-making, washing, baking, medicine, &c. It is obtained from different sources:

- (1.) One is kelp, which contains from 2 to 5 per cent. of it.
- (2.) A second is barilla—the saline ash left after the combustion of certain maritime, not marine, plants (*Salsola soda* and *Salicornia herbacea*), which are cultivated on the shores of the Levant for the sake of the soda they contain. Barilla contains about 18 per cent. of the carbonate.
- (3.) Another source is the native carbonate (frequently a sesquicarbonate), found on the margins of certain bodies of water in Egypt and other parts of Africa, as well as in Mexico and in Hungary. The Egyptian lakes which are the most familiar are called the ‘Natron Lakes,’ and have yielded soda from a very remote period. The nitre of the Bible, which is referred to as having detergent properties, is this natron, or sodium carbonate; not our nitre, potassic nitrate.
- (4.) The greater part, however, of the sodium carbonate used in Great Britain is manufactured from sodium sulphate, which, in its turn, as already mentioned, is procured from common salt by heating it with hydric sulphate.

898. The crude anhydrous sulphate, which is called ‘salt-cake,’ is reduced to powder, and mixed with an equal weight of limestone and nearly as much coal, and heated, with constant

stirring, on the bed of a reverberatory furnace. The sulphate is decomposed by the carbon of the coal, with formation of carbonic oxide and sodic sulphide :



The sodic sulphide then acts upon the limestone (calcic carbonate), and calcic sulphide, together with sodic carbonate, are produced :



The black mass, which is called 'black ash,' is broken up, and lixiviated with warm, not hot, water,* and the solution, when evaporated to dryness, yields a residue, called 'soda-ash.' This residue, when again dissolved in just sufficient hot water, and allowed to cool, forms crystals, which are the common 'washing-soda' of commerce. These are in the form of transparent flat rhomboidal prisms, which contain ten molecules of water of crystallisation, and effloresce in dry air. The salt is readily soluble in water, and has an alkaline taste and action on vegetable colours.

899. *Sodic Hydric Carbonate* (NaHCO_3).—This is the common 'bicarbonate of soda,' and is prepared by passing carbonic dioxide over the carbonate. It has a milder taste and feebler alkaline action than the last salt. It is largely used in the preparation of effervescing powders.

900. *Sodic Sulphide* (Na_2S), which has been referred to already, as prepared from sodic sulphate by withdrawing its oxygen, as a step in the soda process, is also important as one of the ingredients of *lapis lazuli*, from which *ultramarine* is prepared. An artificial ultramarine, rivalling the native pigment in beauty, is obtained by heating sodic sulphide with kaolin (aluminic silicate), sulphur and charcoal. The other sodic sulphides, which resemble those of potassium, are not important.

901. *Sodic Iodide* (NaI) resembles the corresponding salt of

* If water above 43° is used, the calcic sulphide enters into solution as sulphydrate, CaH_2S_2 .

potassium. It occurs in kelp, and is interesting as the source of iodine, under which it has been noticed.

902. All compounds of sodium, when introduced into the flame of a spirit-lamp or Bunsen burner, impart an intensely yellow colour to the flame. This has been sufficiently described already in the chapter on LIGHT (see pages 77–80). This sodium light is entirely cut off by a piece of blue glass.

903. *Tests for sodium in combination.*—A solution of common salt, or of sodic carbonate, is to be prepared, and five test-tubes half filled with it.

(1.) To the first, solution of ammoniac sulphide is added. It will occasion no precipitate.

(2.) To the second, solution of ammonia, and then a drop or two of solution of sodic phosphate. They will also occasion no precipitate.

904. These negative indications only go the length of proving that the salt tested is a compound of potassium, or sodium, or ammonium.

(3.) To the third glass, solution of hydric tartrate is added. No precipitate.

(4.) To the fourth, solution of platinic tetrachloride. No precipitate.

The non-appearance of precipitates with the last two tests proves the salt *not* to be one of potassium.

(5.) To the fifth tube, a little quicklime or caustic potash is added. No odour of ammonia is emitted. The absence of odour proves the salt *not* to be one of ammonium, as will be explained more fully under that substance. And as it has already been shewn not to be a salt of potassium, it must be one of sodium; for the first two tests tried, limited us to sodium, potassium, or ammonium; and the following three tests have rejected the last two bodies, so that we are limited to the first.

905. The solution may now be evaporated to dryness, and its residue examined as to the test it communicates to flame. To avoid this trouble, dry common salt may be taken and heated

at the blow-pipe, or moistened with alcohol and the latter set fire to. In either case, the same bright yellow flame which characterised burning sodium will be observed. It is seen to greatest advantage by throwing sodic nitrate on a cinder-fire; but in all circumstances it is readily noticed, and is greatly more distinct on the small scale than the violet flame of the potassium salts; so that, if one of the latter be mixed with a compound of sodium, and the effect of the mixture on flame observed, the yellow light will be found completely to overpower the violet. This, accordingly, is a delicate and convenient test for dry salts of sodium. There is no very simple *positive* test for them in solution, but they are easily detected by the negative method explained.

RUBIDIUM AND CÆSIUM.

906. These rare metals are chiefly interesting as being the first-fruits of the methods of spectrum analysis systematised by Bunsen and Kirchhoff. The mode of their discovery and the character of their spectra are given in the chapter on LIGHT (par. 227, page 82; see also page 79). Since their discovery in the water of the Durkheim and Nauheim springs, their presence has been recognised in many substances. Rubidium, for instance, has been found in lepidolite, a variety of mica, and in the ashes of beet-root and tobacco. Cæsium has been found to constitute 30 per cent. of a rare mineral called pollux. In their chemical relations, both the metals much resemble potassium, and are only with difficulty separated from it, by taking advantage of the greater insolubility of the double salts formed by their chlorides with platinic chloride, so that, by repeatedly boiling the mixture of the salts with water, the rubidic and cæsic salts are found in the insoluble residue.

AMMONIUM.

| | Formula. | Weight. |
|--------------|----------------------|---------|
| Radicle..... | H_4N | 18. |

907. A compound of nitrogen and hydrogen—namely, ammonia (H_3N)—has been already described (page 204), and it has been mentioned that, when this gas is caused to act upon hydric chloride, a white salt (sal-ammoniac) is formed, which crystallises in cubes, and, in other respects, greatly resembles potassic and sodic chlorides. A similar action occurs whenever a salt of hydrogen (in other words, an ‘acid’) is brought in contact with ammonia: the hydrogen of the former is not evolved, but appears to associate itself more closely with the nitrogen and hydrogen of the ammonia, to form a group of atoms, or compound radicle, represented by the formula H_4N , which can be transferred from one compound to another, like a simple element. It is quite true that from these salts we can obtain ammonia, by acting upon them with many metallic oxides, such as calcic oxide (see the process for preparing ammonia, page 205); but, in most respects, they closely resemble the salts formed by potassium with the same radicles, for instance, in solubility, crystalline form, and behaviour with reagents.

908. These points of analogy naturally led chemists, after the discovery of the decomposition of potassium and sodium salts by the electric current, to try the effect of the same force upon such a salt as sal-ammoniac. When an electric current is passed through a solution of potassic chloride, the negative pole being a globule of mercury (into which the battery-wire dips), the mercury becomes pasty and almost solid, owing to the formation of an amalgam or alloy of potassium and mercury. When, instead of potassic chloride, a solution of sal-ammoniac is taken, a very similar effect is produced. The globule of mercury swells up to 8 or 10 times its former bulk, becoming pasty, and losing much of its brightness; in fact, assumes all the appearance of an amalgam of a metal.

909. Another and easier mode of producing the same effect is the following: A small quantity (about 4 or 5 grms.) of mercury is gently warmed in a tube or porcelain basin, and one or two fragments of sodium added to it. The metals unite with evolution of heat and light, and the resulting sodium-amalgam is placed in a tall, narrow glass, and covered with a saturated solution of sal-ammoniac. It instantly commences to swell up, and undergoes an enormous increase in volume, retaining a certain amount of its metallic lustre, but exhibiting a consistence like that of butter. The amalgam, indeed, provided it be kept under the surface of the liquid, can be moulded into any shape. Its great increase in volume is accompanied by a very trifling one in weight, the augmentation not being more than about one twelve-thousandth part.

910. But this so-called amalgam is not permanent. No sooner is it withdrawn from the solution in which it is formed, than it begins to shrink, giving off bubbles of hydrogen and ammonia, and the mercury soon resumes its original appearance and size. Nor have any means been found of preventing this decomposition, and no one has yet caught a glimpse of the substance which, like hydrogen, every analogy would lead us to consider as a metal.*

911. In spite, however, of the fact that it has never been with certainty isolated (like fluorine), chemists agree to consider salts formed by the union of ammonia with a hydrogen salt, as containing the *quasi*-metallic radicle ammonium, and to write their formulæ in such a way as to shew their analogy to undoubted metallic salts. We shall proceed to consider a few of the more important of these salts.

912. *Ammonic Hydrate*, $(\text{H}_4\text{N})\text{HO}$.—Ammonia dissolves very readily in water (see page 206), and the solution is believed to

* It must be observed that it is extremely doubtful whether this so-called amalgam is anything more than mercury-froth. A not dissimilar froth can be obtained in other ways; and, when the porous mass is subjected to pressure, it collapses almost to the original bulk of the mercury. Equal doubt must be thrown on the reported isolation of ammonium by a German chemist, who obtained a blue liquid by bringing liquefied ammonia in contact with sodium and ammonic chloride.

contain the hydrate, although the latter has never been obtained in a separate form. Solution of ammonia, the *liquor ammonia* of the shops, resembles, in many of its properties, the solution of potassic hydrate. It has a sharp caustic taste, and strong alkaline reaction on reddened litmus and turmeric paper. When added to solutions of most metallic salts, it occasions a precipitate of the metallic hydrate, which in the case of silver, copper, cadmium, cobalt, nickel, manganese, zinc, and magnesium, is soluble in excess of ammonia, a compound being formed in which some or all of the atoms of hydrogen in ammonium are replaced by the metal. (See under COPPER.)

913. *Ammonic Carbonates*.—Ammonia and carbonic dioxide combine in presence of water in several proportions. The 'sesquicarbonate' sold in the shops is believed to be a mixture of 1 molecule of neutral carbonate, $(\text{H}_4\text{N})_2\text{CO}_3$, with 2 molecules of ammonic hydric carbonate, $(\text{H}_4\text{N})\text{HCO}_3$. It is prepared by heating a mixture of powdered sal-ammoniac and chalk in an iron pot provided with a dome-shaped cover. The salt sublimes, forming a white crystalline mass, which gives off ammonia at ordinary temperatures, and constitutes the smelling-salts of the shops. Much of what is sold as smelling-salts is a mixture of coarsely powdered sal-ammoniac and potassic carbonate. The reaction of these on each other leads to a constant evolution of the volatile carbonate, which may be increased at intervals by stirring the mixture, and putting the bottle in a warm place, with the occasional addition of a drop of water, if the contents appear too dry. A solution of ammonic carbonate forms the well-known 'sal volatile,' used in medicine as a stimulant. It is also employed in the laboratory as a test, and is valuable as enabling us to prepare other ammonic salts by neutralising it with various acids. Thus the nitrate may be prepared by adding the carbonate to hydric nitrate, and the acetate and citrate, which are used in medicine, by neutralising the carbonate with hydric acetate (vinegar) or hydric citrate (lime-juice).

914. *Ammonic Sulphate*, $(\text{H}_4\text{N})_2\text{SO}_4$, is now a considerable

article of commerce as a fertiliser, and also in the alum manufacture. It is prepared on the large scale, by neutralising the gas liquor or bone liquor, as well as other liquids containing ammonia, with hydric sulphate, and purifying by crystallisation.

915. *Ammonic Chloride*, $(\text{H}_4\text{N})\text{Cl}$.—This salt has been already referred to (page 204) as the source of ammonia, and its mode of preparation was there indicated. In practice, its manufacture is usually combined with that of sodic carbonate, the crude hydric chloride obtained in the first stage of the process (par. 898, page 360) being led into cisterns containing the gas liquor, and the ammonic chloride crystallised out by evaporation, and purified by sublimation. It is sold in the shops in large, hollow, hemispherical cakes, which owe their shape to the leaden domes or cupola-like covers of the iron pots in which the salt is sublimed. It has in cake a peculiar tough and fibrous structure, which makes it one of the most difficult substances to pulverise. When struck with the pestle, it splits into threads without crumbling into powder. It is one of the few substances which, when heated, pass from the solid to the gaseous state without (under ordinary pressures) becoming liquid. This the student may verify by heating a fragment in a test-tube. The density of its vapour is anomalous, being only half as much as analogy would lead us to expect. It may be obtained in regular crystals, both by sublimation and by evaporation of its aqueous solution. Their shape is the same as that yielded by potassic and sodic chloride, namely, the cube.

916. *Ammonic Sulphydrate*, $(\text{H}_4\text{N})\text{HS}$.—This salt, often called *ammonic sulphide*, which is much used in analysis, is prepared by passing a current of hydric sulphide through dilute solution of ammonia, until a sample of the liquid gives no white precipitate when tested with solution of magnesian sulphate. An equal volume of the same solution of ammonia is then added, and the solution is ready for use as a test. It is employed to precipitate metals from their solutions, as sulphides or sulphydrates, which are distinguishable from each other by their colour, and their solubility in acids, water, or in a solution

of ammoniac sulphhydrate itself. Its solution decomposes spontaneously when long kept, becoming yellow owing to the formation of higher sulphides, while ammonia escapes, and eventually ammoniac sulphate is formed.

917. *Tests for Ammonium in combination.*—We have already mentioned fully the characters by which uncombined ammonia may be recognised. We have now to state the mode of identifying its derivative ammonium, when in combination with other radicles. A solution of any salt of ammonium, but preferably the chloride (about 5 grms. in 50 c.c. of water), may be taken, and separate portions tested as follows:

(1.) To the first, ammoniac sulphhydrate is added. No precipitate is given.

(2.) To the second, solution of sodic phosphate, with a little ammonia, is added. No precipitate. These negative results prove, as mentioned already, the salt in solution to be a compound of potassium, sodium, or ammonium.

(3.) A third portion is tested with solution of hydric tartrate. No precipitate occurs, even on shaking the mixture and allowing it to stand. The salt, therefore, is not one of potassium.

(4.) To another portion, solution of platinic chloride is added. A yellow crystalline precipitate is gradually formed. The salt, therefore, is not one of sodium. It cannot, accordingly, be anything but a salt of ammonium. But this may be further proved by positive tests, such as the actual evolution of ammonia from it.

(5.) Another portion is mixed with a little quicklime or caustic potash, and warmed. The characteristic odour of ammonia will be at once perceived. A piece of moistened red litmus-paper, or yellow turmeric-paper, is held in the tube, care being taken that it does not touch the liquid. The former becomes blue, the latter brown. Further, a glass rod dipped in hydric chloride may be held in the tube for a moment, when white fumes of ammoniac chloride will be observed.

918. There is no distinctive blow-pipe test for ammoniac salts. The great majority of them, when heated, are volatilised with

or without decomposition. If ammoniac carbonate, sulphate, or nitrate is heated in an iron spoon, or on a piece of platinum foil, over a lamp, they are in a few seconds completely dissipated, and are thus at once distinguished without further test from salts of potassium or sodium, none of which are volatilised below a red heat. Compounds of ammonium, however, with the less volatile acid radicles, such as the phosphate, give off only ammonia, when heated, so that a residue of the acid is left.

919. One other extremely delicate test for ammoniacal salts must be mentioned, as it is often used for the detection of these salts in rain-water. A solution is made by adding solution of potassic iodide to solution of mercuric chloride until the precipitate of mercuric iodide is nearly all re-dissolved. An equal volume of solution of potassic hydrate is then added, and the mixture allowed to stand until it is clear. When a few drops of this solution are added to an ammoniac salt, a reddish brown precipitate is formed. Even if the liquid to be tested contains only one-millionth part of the ammoniac salt, the presence of this may be recognised by the appearance of a red coloration when the tube is held against a sheet of white paper. This is called Nessler's test, from the chemist who proposed it.

LITHIUM.

| | Symbol. | Weight. | |
|------------|---------|---------|-----------------|
| Atom | Li | 7 | Density = 0.59. |

920. This comparatively rare metal forms a link between the metals already described and those which follow. In most respects it resembles potassium, but its carbonate is, like that of silver, barium, &c., scarcely soluble in water. It occurs in several minerals, such as spodumene, or lithia-felspar, and lepidolite or lithia-mica, and also in the water of certain springs, especially one in Cornwall. The spectroscope has shewn that it is a very widely distributed element, occurring in sea-water, in tobacco, and in many soils.

921. Lithium is obtained by passing an electric current through lithic chloride, fused over a lamp. It is interesting as being the lightest metal known, only a little more than half as heavy as water. It quickly oxidises in the air, and decomposes water, but not with such violence as potassium or sodium. All the compounds of lithium, when heated in the flame of a spirit-lamp or Bunsen burner, volatilise and colour the flame a beautiful crimson. The light, when examined in the spectro-scope, is seen to consist of two bright bands, one in the red between B and C, and the other in the orange near D (see fig. 21, page 79).

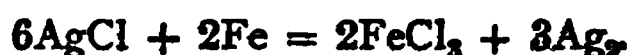
SILVER.

| | Symbol. | Weight. | |
|-----------|---------|---------|-----------------|
| Atom..... | Ag | 108 | Density = 10.5. |

922. The metal silver is introduced here mainly on the evidence of its atomicity. Almost all its properties would lead us to classify it rather with lead and mercury than with the alkaline metals. It has been known and valued from very early times, and many of its compounds were obtained and examined by the alchemists, who called it Luna, from its brilliancy, whence the name of 'lunar caustic,' for silver nitrate, has descended to us. Its Latin name is *argentum*, and from this the symbol for its atom, Ag, and the nomenclature of its salts adopted in this book, are derived.

923. *Sources*.—Silver is found native in Saxony, Peru, and Mexico, sometimes crystallised, but more often in fibrous moss-like masses interspersed in gneiss and granite rocks. Its most abundant ore is the sulphide forming the mineral argentite, from which much of the silver of commerce is obtained. It also occurs associated with lead and sulphur in certain kinds of galena, a mineral usually worked as an ore of lead, but often containing enough silver to be worth extraction, especially as, by a process to be described under LEAD, the minute proportion of silver in the ore can be concentrated and obtained in the form of a rich alloy with lead.

924. *Extraction.*—The native sulphide is ground to a coarse powder, mixed with salt, and roasted at a high temperature. The antimony and arsenic in the ore are thus volatilised, and the silver is obtained as chloride, sodic sulphide and sulphate being also formed. The finely powdered residue is then placed in large casks together with some scraps of iron and a sufficient quantity of water, and the casks are violently agitated for many hours, during which time the argentic chloride is gradually decomposed by the iron, with formation of ferric chloride and metallic silver.



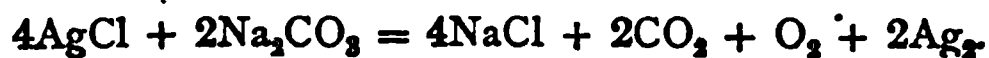
A certain proportion of mercury is now placed in the casks, and forms an alloy or amalgam with the silver, from which it is afterwards distilled off, leaving the silver nearly pure.

925. The rich alloy of silver and lead, obtained in the lead manufacture from the smelting of argentiferous galena, is subjected to a process called cupellation, which depends upon the different affinities of lead and silver for oxygen. The alloy is placed in a 'cupel,' or large porous basin of dried bone-ashes, supported on the bed of a reverberatory furnace. A current of hot air and flame is allowed to play upon the mass, when the lead combines with oxygen, forming litharge (plumbic oxide), which fuses and floats on the surface of the silver, the latter remaining quite unaltered. The litharge is drawn off through an aperture at the end of the furnace, the last portions being absorbed by the porous cupel. Towards the end of the operation, the melted mass presents the most brilliant colours, owing to thin films of litharge floating on its surface, and finally a liquid mass of pure silver remains on the cupel. When this has cooled to the solidifying point, a curious phenomenon shews itself. Silver has the property of absorbing a large amount of oxygen at a high temperature, which is given off again as the temperature falls; and thus the surface of the mass is ruffled by the escaping gas, which throws up crater-like ridges as it forces its way through the yielding metal.

926. *Properties.*—Pure silver has a brilliant white lustre, and

is the best-known conductor of heat and electricity. It is very soft and extremely malleable and ductile; it can be beaten into leaves only $\frac{1}{4000}$ th of a millimetre in thickness, and drawn into wire of which 2600 metres weigh only 1 gramme. It is indeed a typical metal, possessing the metallic characters in the highest degree. It melts at a bright red heat, and does not lose its lustre by oxidation; hence it is extensively used for jewellery and plate (the latter being the same word as the Spanish 'plata,' silver), and also for coinage. For these purposes the pure metal, which is itself too soft to stand wear and tear, is always alloyed with various proportions of copper, the 'standard silver' for the English coinage containing 7.5 per cent. of copper.

927. Silver may be obtained pure for chemical purposes by the following process, which the student may repeat with any fragment of sterling silver, such as a defaced coin. The metal is dissolved in pure slightly diluted hydric nitrate, in which it will disappear with great rapidity, with evolution of much nitric oxide. The solution will have a green colour, from the copper with which silver is purposely alloyed, and provided the hydric nitrate has been perfectly free from chloride, a small amount of black powder will generally remain undissolved. This is gold, which it was not worth while to separate from the silver when it was reduced from its ore. To the clear liquid, which contains argentic and cupric nitrates, a solution of common salt is added as long as a precipitate falls. This is the insoluble argentic chloride, the copper remaining in solution. The chloride is washed, dried, and melted in a crucible, along with anhydrous sodic carbonate. Sodic chloride and metallic silver are the results:



The mass should be stirred with an iron rod, and the temperature raised to a very bright red, in order to unite the scattered particles of silver into one mass, which will be found, after the operation, at the bottom of the crucible as a brilliant button.

928. The reduction may be more easily effected in the following way. The argentic chloride is to be separated from the soluble cupric chloride by filtration and repeated washing with water on the filter (par. 279, page 107). It is then placed in a basin or beaker, covered with dilute hydric sulphate, and a strip of zinc placed in contact with it. The hydrogen evolved unites with the chlorine of the chloride, leaving metallic silver, and the action gradually spreads outwards, until, after the lapse of several hours, a gray spongy mass of reduced silver is left, while the liquid contains zinc chloride and sulphate. The silver must be well washed with dilute hydric sulphate, and may then be fused, with addition of a little borax, into a globule, or dissolved in hydric nitrate, as required.

929. *Argentic Nitrate* (AgNO_3).—This is the most important salt of silver, and from it most of the other salts are obtained. It is prepared by dissolving pure silver in hydric nitrate, and concentrating the solution. Flat, tabular crystals will be formed, which melt, without decomposition, below a red heat, and when cast into sticks, form the 'lunar caustic,' used for surgical purposes, to remove diseased tissues. It owes its powerfully caustic properties to its tendency to form compounds with all kinds of organic matter. These compounds, when exposed to light, become black, owing to reduction of the silver. The ordinary 'marking ink' for linen is a solution of argentic nitrate, thickened with gum-arabic; and when it is placed on linen, and exposed to a moderate heat, a decomposition takes place like that produced by light, and a black mark is left, which no washing will remove. Stains produced by silver salts may be removed most effectually by the application, first, of a solution of potassic iodide, and then of a solution of potassic cyanide; but the latter must be used with caution, as it is very poisonous.

930. *Argentic Oxide* (Ag_2O).—Silver does not, except under the peculiar circumstances noticed in par. 926, unite directly with oxygen, differing totally in this respect from the metals we have hitherto considered. The oxide is, however, obtained by

addition of potassic hydrate to a solution of argentic nitrate, the hydrate, it would seem, not being formed.



It is a brown substance, slightly soluble in water, the solution having an alkaline reaction, and absorbing carbonic dioxide from the air, like potash. It is readily decomposed into silver and oxygen at a temperature a little above 100° . It dissolves with facility in solution of ammonia, and this solution, if it contains no excess of ammonia, is decomposed, with separation of metallic silver, when mixed with many organic substances, such as a tartrate or milk sugar. This is the basis of the processes for silvering mirrors, and specula for telescopes; as the silver is deposited in a coherent film, which will even bear polishing with a wash-leather dipped in rouge.

931. In contrast to its slight affinity for oxygen, silver combines most readily with sulphur. A surface of polished silver becomes rapidly tarnished in presence of many sulphur compounds, such as hydric sulphide. The blackening of silver egg-spoons is due to the presence of sulphur in the egg; and silver ornaments, plate, &c., are soon tarnished in rooms lighted with gas, owing to the traces of hydric sulphide in the gas.

932. *Argentic Chloride* (AgCl).—This salt, as has been mentioned under CHLORINE, is formed when any soluble chloride is added to a solution of argentic nitrate. It forms a white, flocculent precipitate, which fuses unchanged when heated, and solidifies, on cooling, into a substance resembling horn in appearance and softness, and formerly called 'horn-silver.' Argentic chloride is insoluble in hydric nitrate, but readily dissolves in ammonia, in potassic cyanide, and in sodic hyposulphite. The precipitated salt quickly changes colour when exposed to light, becoming eventually dark purple or nearly black. Chlorine is given off; but it has not yet been ascertained whether a subchloride (Ag_2Cl) is formed, or whether reduction to metallic silver at once takes place. This

decomposition takes place much more readily and completely in presence of organic matter, and forms the basis of the principal photographic processes now in use.

933. To begin with the simplest and most direct mode of sun-printing. A sheet of paper is coated on one side with a solution of albumen containing a soluble chloride, usually ammoniac or baritic chloride (about 3 grms. of the salt in each 100 c.c. of the solution). When the film is perfectly dry, it is floated (in a room lighted only by a candle, or a window of yellow glass) upon a solution of argentic nitrate (about 12 grms. of the salt in each 100 c.c. of water), and thus a fine layer of argentic chloride is obtained, in contact with organic matter and a large excess of argentic nitrate. The paper, when dry, is ready for use; and, when exposed to the light, speedily blackens all over, the chlorine separated from a particle of chloride decomposing another portion of nitrate, with formation of more chloride, and so on. If parts of the paper are protected from light, for example, by laying upon the film a piece of perforated zinc, or letters cut out of thick black paper, the whole being pressed between two plates of glass to keep it flat, a white picture on a black ground is obtained. But this picture is not permanent; it would, if brought into light, shortly become merged in one uniform black, and hence the unaltered chloride and nitrate must be removed by soaking the paper, first in water, and then in a solution of sodic hyposulphite (about 10 grms. in each 100 c.c.). As, however, the picture is much reduced in intensity during this 'fixing,' as it is termed, the paper, before being placed in the hyposulphite, is soaked in a very dilute alkaline solution of auric chloride. The effect of this 'toning' process is to replace the reduced silver by metallic gold (the more electropositive by the less electropositive metal, just as iron is replaced by copper), and to give a picture of greater permanency, more agreeable in tint, and which is not materially reduced in intensity by the subsequent action of hyposulphite. In the last place, the paper must be thoroughly washed until all traces of soluble salts are removed.

934. By the above process, from half an hour to three or four hours are required to obtain a picture, and it is therefore quite inapplicable for taking views or portraits by throwing the image formed by a lens upon the prepared paper. For such purposes a different process is used, the principle of which was discovered by M. Daguerre in 1839. When argentic iodide is exposed to light in presence of an excess of argentic nitrate, it slowly darkens in colour, undergoing a change which is probably not chemical (since hydric nitrate dissolves no silver from it), but physical, an allotropic modification being formed. Whatever the actual change is, it is certain that the iodide, by a very short exposure to light (long before any visible darkening has taken place), has acquired the power of hastening the decomposition of unstable silver salts, and attracting the deposit of reduced silver. This property, which is shared by argentic bromide, is the basis of most 'development' processes in photography. A glass plate is covered with a film of collodion (a solution of gun-cotton, or pyroxyline, in a mixture of ether and alcohol), in which an iodide (preferably cadmic iodide), together with a variable proportion of a bromide, has been dissolved. Before the film is quite dry, it is placed for a few minutes in a solution of argentic nitrate, and thus a thin layer of argentic iodide and bromide is formed on the glass. While the porous film is still moist, and retains the excess of argentic nitrate, it is exposed to the image formed by a lens in a dark box, or 'camera,' for a period varying from one-tenth of a second to half a minute. The yellow film of iodide appears quite unchanged when removed from the camera; but when a solution of a reducing agent, such as ferrous sulphate or hydric pyrogallate (pyrogallie acid), slightly acidified with hydric acetate, is poured over it, a brown deposit is soon seen to form upon the parts where the high lights of the image fell. The ferrous sulphate reduces the excess of argentic nitrate in the film, and the reduction takes place most rapidly at the parts which have been exposed to light. Thus any amount of opacity may be obtained by the use of successive portions of solution

of ferrous sulphate mixed with a drop or two of argentic nitrate, care being taken to wash off the solution as soon as much turbidity, indicative of general decomposition, shews itself. Finally, the argentic iodide, which has now served its purpose, is dissolved away by sodic hyposulphite, and the film thoroughly washed. We have now a reversed picture, or 'negative,' in which the lights of the original image are represented by deposits of silver, varying in opacity according to the intensity of the light, while in the shadows the film is perfectly transparent. This negative is now, after being varnished, placed in contact with a piece of prepared paper, and printed from as described in the last paragraph.

935. *Tests for Silver.*—Silver, as will be seen from the table at page 349, is placed, for analytical purposes, in a group quite distinct from potassium, sodium, and ammonium, and is one of the first metals which the analyst detects in his course of work. Separate portions of a dilute solution of argentic nitrate may be examined as follows :

(1.) To the first portion a little hydric chloride is added. A white curdy precipitate of argentic chloride is formed, rapidly subsiding when shaken. The liquid in which the precipitate is suspended is divided into two portions. To the one, hydric nitrate is added; the precipitate remains unaltered. To the other, solution of ammonia is added, which readily dissolves the precipitate, forming a clear solution, which becomes turbid again when hydric nitrate is added.

(2.) To the second portion, solution of hydric sulphide is added. A black precipitate of argentic sulphide is formed, insoluble in dilute hydric nitrate, but decomposed by the strong acid, on boiling.

(3.) The salts of silver, when heated on charcoal with sodic carbonate before the blow-pipe, yield a brilliant metallic malleable bead, while no crust of oxide is formed on the surrounding charcoal.

*Section III.—Diatomic Metals.—Metals of the Alkaline Earths :
Calcium, Strontium, Barium, Magnesium.*

CALCIUM.

| | Symbol | Weight. | |
|-----------|--------|---------|-----------------|
| Atom..... | Ca | 40 | Density = 1.57. |

936. *Occurrence.*—The element calcium is found in great abundance, and in a variety of combinations. As a carbonate it constitutes the extensive strata of limestone, marble, and chalk, and also the beautifully crystallised minerals, arragonite and Iceland spar. As a sulphate, it occurs in gypsum, alabaster, and selenite. Fluorspar, as already noticed (page 284), is a compound of calcium with fluorine. As a phosphate, it forms the principal inorganic constituent of the bones of animals; while shells almost entirely consist of calcic carbonate.

937. The metal itself is rarely seen, and is prepared by passing a galvanic current through fused calcic chloride. It is a yellowish-white metal, intermediate in hardness between lead and gold, and readily combines with the oxygen of the air or water. It must therefore, like potassium, be preserved in naphtha. It derives its name from the Latin term for lime, *calx*, from which our English word calcareous is derived.

938. *Calcic Oxide*, or *Quicklime* (CaO), is obtained by heating limestone (calcic carbonate) with coal to redness in a lime-kiln or open fire. The carbonic dioxide is totally expelled, and the oxide is left:



Pure lime, such as may be procured by heating statuary marble or Iceland spar, forms a white, brittle, porous mass, which is highly caustic, and about three times heavier than water. It is infusible at the highest attainable temperature, and is used to form crucibles in which platinum is melted. When strongly heated in the oxyhydrogen flame, it glows with a most brilliant light (see page 186). If sprinkled with water, it first absorbs

it, and then combines with it, forming a definite, dry hydrate. This process is called the slaking or slacking of lime, in allusion to its drinking up, as it were, the water poured on it. The quicklime, or lime-shell, during the process of slaking, evolves much heat, and finally crumbles into a fine powder, which is the hydrate, CaH_2O_2 . The temperature produced is sufficiently high to char and even to kindle wood. Carts conveying lime-shell have been set on fire in this way by a casual shower of rain, and similar accidents have occurred to sailing-vessels from accidental leakage.

939. If calcic hydrate be exposed to a red heat, it parts with its water, and returns to the state of unslaked lime. Lime is often slaked in the laboratory, and then unslaked by heating it, as the most convenient way of obtaining it in the state of fine powder.

940. Calcic hydrate is soluble in water to a small extent, and, curiously enough, is more soluble in cold than in hot water. One litre of water dissolves, at 15° , 1.73 grm. of calcic hydrate; while at 100° , the same volume only dissolves 0.83 grm. This solution forms the well-known lime-water which is used in medicine, and kept in the laboratory as a test for carbonic dioxide. Lime-water is harsh to the taste, acrid, and caustic, as solutions of potass and soda are. Like them, it turns red litmus blue, purple cabbage green, and yellow turmeric brown. It also resembles them in its affinity for carbonic dioxide, but differs from them in the fact that the carbonate formed is insoluble.

941. The two chief uses of lime are in the formation of building-mortar, and as an application to increase the fertility of the soil. Ordinary mortar consists of lime made into a paste along with sand, and sometimes chopped hair. The object of the sand is to prevent the irregular contraction and cracking of the lime as it dries. The hair binds together the lime, and prevents its crumbling when very dry.

942. During the process of hardening, a certain amount of carbonic dioxide is absorbed by the mortar from the air, but in

no case does the lime return entirely to the state of carbonate. The truth of this statement may be verified by mixing mortar from any old building with water, and then adding hydric chloride, which will be found to occasion only a slight effervescence. A certain amount of calcic silicate also appears to be formed.

943. Hydraulic mortar, or that employed for cementing the piers of bridges and other structures which are exposed to the action of water, consists of a natural or artificial mixture of limestone and ferruginous clay—that is, calcic carbonate and aluminic silicate containing iron. This is burned in a lime-kiln, and reduced to powder. When mixed with water, it sets as quickly as stucco, and finally becomes as hard as stone, in consequence of the formation of hydrated calcic and aluminic silicates. Portland cement and Roman cement are mortars of this description.

944. The action of lime in fertilising soils is still matter of dispute. This much, however, appears to be certain: the efficacy of lime is most striking—first, on lands which are unfertile owing to excess of vegetable matter, such as bog, turf, or peat soils; and secondly, in stiff clay soils. It improves the first, by causing the rapid decomposition of the excess of vegetable matter, so that the saline or mineral matter in the soil comes to bear a proportion to its vegetable or organic constituents, compatible with the healthy growth of plants in it. On clayey soils, lime appears to act beneficially by liberating the alkalies, especially potash. These are contained in the clay in union with its silica and alumina, so that rain-water cannot dissolve them and carry them into the tissues of plants. The lime, by combining with the silica and alumina, as it does in the hydraulic mortar, sets free the alkalies, which are then available for the nourishment of vegetables. The lime in this case is spread upon the land in autumn or winter, and the ground is not sown till spring.

945. *Calcic Carbonate* (CaCO_3) occurs in nature in various forms, as noticed above. Its purest form is Iceland spar, which

is found in perfectly transparent rhombohedra (see fig. 8, B, page 38), and is celebrated for the striking way in which it exhibits the double refraction of light. When a ray of light falls on a natural face of the crystal, it is divided into two rays, which pass through the interior in different directions, and are seen to be widely separated on emergence. This may be easily shewn by placing a piece of Iceland spar upon a page of a book, or upon a sheet of writing-paper, on which a line or a dot has been made. Two images of the single dot will be seen, which seem to revolve round each other when the crystal is turned. All transparent crystals belonging to any other system than the regular system (see page 36) possess this property, but none so markedly as Iceland spar. Calcic carbonate also occurs in many other crystalline forms, all belonging either to the rhombohedral system, or to the right prismatic system, as arragonite.

946. Calcic carbonate is insoluble, or nearly so, in pure water, but it dissolves readily in water containing carbonic dioxide, a soluble calcic hydric carbonate being then formed :



The solution of this latter is readily decomposed by heat, or by mere exposure to the air—a fact which has already been mentioned as accounting for the incrustation formed in steam-boilers (page 188). Some springs, which are called petrifying springs, contain the salt in such quantity as to deposit it readily upon objects placed in them. It is believed that the large masses of oolite, a granular limestone, were formed by the precipitation of calcic carbonate from solution upon minute nuclei, so as to form aggregations of small grains. Stalactites were similarly formed, and also the tufa and travertino of Italy, so valuable for building purposes.

947. When a sufficient quantity of lime-water is added to such a solution, the whole of the calcium is precipitated as neutral carbonate :



This is the basis of Dr Clark's process for rendering 'hard' waters soft and fit for washing purposes. The water is let into large tanks, where it is mixed with the proper proportion of lime-water, and allowed to settle. A perfectly clear soft water is thus obtainable, and the process has been proved to succeed well on the large scale.

948. *Calcic Sulphate* (CaSO_4).—This important salt occurs in nature occasionally anhydrous, and is then called anhydrite. It is much more abundant in combination with two molecules of water, $\text{CaSO}_4 + 2\text{H}_2\text{O}$. In this state it is called *gypsum*. The finer transparent varieties form the alabaster of the artist, and the selenite of the mineralogist. When gypsum is cautiously heated till it parts with the greater portion, but not the whole, of the water it contains, it forms plaster of Paris, or burnt stucco. When this, in the state of powder, is made into a paste with water, it quickly forms a solid mass, or, as it is technically called, *sets*. In setting, the stucco takes back the water it was deprived of when heated, evolving heat in so doing, and returning to the same chemical state as the original gypsum. If calcic sulphate be deprived by heat of the whole of its water, it will not set when moistened, and it is scarcely possible to burn set stucco so as to make it set again.

949. Calcic sulphate appears as a thick pasty precipitate when hydric sulphate is added to a strong solution of any salt of calcium. It forms a striking experiment to add hydric sulphate to a saturated solution of calcic chloride. So much of the sulphate is produced that the whole liquid appears to solidify, and the vessel may be turned upside down without anything escaping.

950. Notwithstanding the fact just mentioned, calcic sulphate is soluble in water to the extent of one part by weight of the salt in 460 of water. Such a solution is kept in the laboratory as a test, and will presently be referred to, as enabling us to distinguish the alkaline earths from each other. Permanently hard waters, which are not improved by boiling, generally contain calcic sulphate. The calcium may be got rid of by the

addition of sodic carbonate, which precipitates it as carbonate, leaving sodic sulphate in solution, a salt which does not act upon soap.

951. *Calcic Phosphates*.—Several of these compounds are known, the most important of which is that which occurs in bones, and is distinguished as the bone-earth phosphate (tricalcic phosphate), $\text{Ca}_3(\text{PO}_4)_2$. It has been already referred to under PHOSPHORUS, as also the superphosphate, $\text{CaH}_4(\text{PO}_4)_2$, which is largely employed as a manure.

952. *Calcic Hypochlorite*, the chief constituent of bleaching powder, is more important as a compound of chlorine than as a calcic salt. It has been described under CHLORINE.

953. *Calcic Chloride* (CaCl_2), which must not be confounded with the last-named salt, is obtained as a residue in the process for preparing carbonic dioxide by dissolving marble in hydric chloride, and is produced in the course of other chemical processes on the large scale. It is extremely deliquescent, and, when fused or, better, dried at a temperature of 200° , it is much used in the laboratory as an absorbent of moisture. A tube filled with fragments of it is employed for drying gases (not, however, ammonia, which is rapidly absorbed by it), and also for collecting the water produced during the analysis of an organic substance. In the crystallised condition, when mixed with snow, it forms a very powerful freezing mixture.

954. The only other important calcic salts are the fluoride, which occurs as fluorspar, and has been described under FLUORINE; and the phosphide, which has been mentioned in speaking of HYDRIC PHOSPHIDE.

955. The tests for calcium will be given after the other metals of the group have been described.

956. When a volatile calcic salt is held on platinum wire in the flame of a Bunsen burner, the flame acquires a bright orange tint. In the spectroscope, a series of bright lines are seen, forming a much more complicated spectrum than the metals hitherto considered (see fig. 21, page 79). Of these,

a green line and an orange line, about equal distances on either side of the sodium line, are the most characteristic.

STRONTIUM.

| | | | |
|-----------|---------|---------|-----------------|
| | Symbol. | Weight. | Density = 2.54. |
| Atom..... | Sr | 87.5 | |

957. This metal derives its name from Strontian, in Argyleshire, in the lead-mines of which it is found as carbonate. It also occurs as sulphate in fine prismatic crystals, forming the mineral celestine. It is obtained from its chloride in the same manner as calcium, and closely resembles the latter in properties.

958. *Strontic Oxide* (SrO).—This cannot be readily prepared by heating the carbonate to redness, as in the case of calcium, since the salt is only decomposed at an extremely high temperature. It is obtained by the decomposition of the nitrate, which, when thrown into a red-hot crucible, fuses and gives off nitric peroxide and oxygen, leaving a white porous residue of strontic oxide:



This substance, when water is poured upon it, slakes like lime, forming strontic hydrate, SrH_2O_2 , which is much more soluble in water than calcic hydrate, but otherwise much resembles the latter in properties.

959. *Strontic Nitrate*, $\text{Sr}(\text{NO}_3)_2$, is the only important strontic salt, and is made by dissolving the native carbonate in hydric nitrate. Strontic chloride (SrCl_2) is similarly prepared. With either of these bodies, the student may observe the only character of the strontia compounds which can be said to be of much interest. They communicate to flame a splendid crimson colour, which leads to their employment in the arts for the production of red signal-lights and fireworks. This property may be well observed by throwing a large spoonful of strontic nitrate into a cinder-fire, or, still better, by preparing what the pyrotechnists call red fire. It consists of strontic nitrate, forty

parts by weight ; flowers of sulphur, thirteen ; potassic chlorate, five ; antimonious sulphide, four ; all in fine powder. The potassic chlorate must be pounded separately, and the materials mixed by gentle stirring in a wooden bowl or mortar. If pounded together, dangerous explosions will happen. The mixture, if taken in any quantity, must be fired in the open air, as it produces a large volume of sulphurous anhydride. It is liable to ignite spontaneously, and should, therefore, not be prepared until wanted for immediate use. For an experiment within doors, a strontic salt may be moistened with alcohol, and the latter set fire to. The chloride does better than the nitrate for this purpose, and the effect is very fine if a sheet of paper be kindled after being immersed in the solution.

960. The red light may also be witnessed by heating the strontic chloride in the flame of a Bunsen burner or blow-pipe. When examined in the spectroscope, the light is seen to consist of five or six lines in the red, and (if the high temperature of the blow-pipe flame is used) of one line in the blue. A diagram of the spectrum is given in fig. 21, page 79.

BARIUM.

| | Symbol. | Weight. |
|-----------|---------|---------|
| Atom..... | Ba | 137 * |

961. *Occurrence.*—Barium occurs in nature in combinations analogous to those of strontium, namely, as carbonate in the mineral witherite, and as sulphate in barite, or ‘heavy spar.’ The name barium is derived from the Greek adjective βαρύς (barus), heavy, in allusion to the remarkably high density of its compounds. The metal has been obtained, by the electrolysis of fused baric chloride, as a light yellow powder, which rapidly oxidises in the air and decomposes water.

962. *Baric Oxide* (BaO).—This, which is generally called baryta or barytes, is prepared by heating baric nitrate or iodate

* The student should notice the curious relation between the atomic weights of the members of this group, similar to that seen in the chlorine group. The atomic weight of strontium is almost exactly a mean between the atomic weights of calcium and barium.

to full redness in a crucible, the decomposition being similar to that mentioned under STRONTIUM. The anhydrous oxide forms a gray porous solid, which slakes like lime when water is poured upon it, baric hydrate (BaH_2O_2) being formed. The latter is more soluble in water than strontic hydrate, dissolving in 2 parts of hot, and 20 of cold water. If boiling water is saturated with it, the solution deposits, as it cools, a crystalline hydrate, the composition of which is expressed by the formula, $\text{BaH}_2\text{O}_2, 8\text{H}_2\text{O}$. The liquid which yields these is a saturated cold solution of the hydrate, called baryta-water, and is analogous in properties to the alkaline hydrates, possessing a harsh acrid taste, caustic and poisonous properties, and acting on colouring matters like an alkali. It is at least as delicate a test for the presence of carbonic dioxide as lime-water, and is also used in the laboratory for precipitating various metallic hydrates, such as magnesian hydrate, for which it is especially adapted, since (1) its solution is always free from carbonate; (2) it does not, when in excess, redissolve the precipitated hydrates.

963. *Baric Peroxide* (BaO_2).—When baric oxide is heated to low redness in a tube, and oxygen or air led over it, each molecule of the oxide takes up an additional atom of oxygen, forming the peroxide. It is remarkable that when the heat is raised to full redness, the additional oxygen is given off, and baric oxide again formed; and it has been proposed to prepare oxygen on the large scale by passing air over heated baryta, and then (the current of air being stopped) raising the heat until the absorbed oxygen is given off. When the baryta has slightly cooled, more air is passed over it, and the process repeated.

964. An easier mode of preparing baric peroxide is to mix baryta with four times its weight of potassic chlorate, and heat the finely powdered mixture to low redness in a crucible. An incandescence is observed to pass through the mass, and a mixture of potassic chloride and baric peroxide is obtained, from which the potassic salt may be washed out by water.

965. Baric peroxide is a white substance, scarcely soluble in water, but readily soluble in hydric chloride, and reprecipitated

as a hydrate from this solution on addition of baryta-water in excess. The solution, when it contains excess of hydric chloride, is moderately permanent, and possesses most remarkable powers both of oxidation and reduction. These it probably owes to the presence of hydric peroxide (H_2O_2), since all the barium may be precipitated by addition of hydric sulphate, without altering the peculiar properties of the solution. It will be convenient to defer the examination of these properties until the other compounds of barium have been described (see par. 968, page 388).

966. *Baric Nitrate*, $\text{Ba}(\text{NO}_3)_2$, and *Baric Chloride*, BaCl_2 , are prepared by dissolving the native carbonate (witherite) in hydric nitrate and hydric chloride respectively. When the carbonate cannot be procured, baric sulphate, a much more abundant mineral, is reduced to powder, and heated with ground coal until it is reduced to sulphide (BaS). This latter is then taken instead of the carbonate for decomposition by the acid. Thus, in the case of hydric nitrate,



These salts are employed, in solution, as tests of the presence of a sulphate, as mentioned under SULPHATES. The nitrate is also used in the preparation of green fire, which is made in the same way as the red fire (par. 959), baric nitrate being substituted for strontic nitrate.

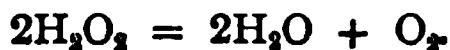
967. Compounds of barium (those, at least, which are volatile, such as the chloride) impart a green colour to flame. To observe this it is best to employ the blow-pipe flame, since that of the Bunsen burner is scarcely hot enough. The spectrum of this flame (see fig. 21, page 79) is very beautiful, but complicated, consisting of a series of green bands, two of which are not far from the solar line E, besides several yellow and orange bands between D and C. Many of these lines have been proved to coincide with solar lines, shewing that barium vapour exists near the surface of the sun.

968. *Hydric Peroxide* (H_2O_2).—A short account of this substance is given in this place, chiefly because the compound from which it is prepared has just been described. When baric peroxide is suspended in water, and a current of carbonic dioxide passed through the liquid, the barium is separated as insoluble carbonate, and hydric peroxide remains in solution.



When the solution is placed over a dish of hydric sulphate in an exhausted receiver, it gradually gives off water, and finally a liquid is left resembling water in appearance, and giving off torrents of oxygen when slightly warmed. This is hydric peroxide—a compound which is rarely seen in a pure condition, but the properties of which may be shewn by taking the solution obtained by adding moist baric peroxide to dilute hydric chloride (1 part acid to 4 of water), care being taken to keep the acid in excess, otherwise decomposition at once sets in. A slight excess of dilute hydric sulphate is then added, the baric sulphate allowed to subside, and the clear liquid decanted.

(1.) When the solution is heated, or when a little spongy platinum is dropped into it, oxygen gas is evolved:



(2.) The solution bleaches vegetable colours, such as indigo, oxidising a part of their hydrogen to form water.

(3.) When a little is added to hydric iodide (or an acidified solution of potassic iodide), iodine is liberated, colouring the liquid yellow, and giving the usual blue colour on addition of starch.

(4.) Another interesting oxidation effected by this substance will be given under CHROMIUM.

969. Hydric peroxide, however, will not only oxidise—it will, in certain cases, produce exactly the reverse effect, and withdraw oxygen from substances.

(1.) When some of the solution is poured on moist argentic oxide, oxygen is evolved, and metallic silver is obtained:



The bearing of this on the constitution of the molecule of oxygen is explained in par. 316, page 122.

(2.) On adding a little hydric peroxide to a solution of potassic permanganate, the deep purple colour of the latter disappears, and a manganous salt is formed, with evolution of oxygen.*

MAGNESIUM.

| | Symbol. | Weight. | |
|-----------|---------|---------|-----------------|
| Atom..... | Mg | 24.5 | Density = 1.74. |

970. *Occurrence.*—Magnesium exists in nature abundantly as carbonate, generally associated with calcic carbonate in the form of dolomite, or magnesian limestone, in Yorkshire and Somersetshire. It is also found in many volcanic rocks, being a constituent of various silicates, as hornblende, talc, and serpentine. Sea-water contains magnesian salts; and some mineral springs, such as those of Epsom, yield considerable quantities of magnesian sulphate, commonly called Epsom salts. Magnesium affords a good illustration of the way in which natural, well-defined groups are connected together by intermediate links. In some of its properties, it resembles barium, strontium, and calcium, while others would lead us to associate it rather with zinc and cadmium. The points of difference and analogy should be noted by the student in the course of his reading, and drawn out in detail.

971. The metal magnesium was formerly obtained, solely as a curiosity, by the electrolysis of its fused chloride. Within the last few years, however, it has been procured in considerable quantity by decomposing its chloride by sodium. A mixture of 6 parts of magnesian chloride, 1 part of potassic chloride, 1 part of fluorspar, and 1 part of sodium in small fragments, is placed in a crucible and heated to redness. A violent action takes place, and the fused mass, after being stirred with an iron rod, to unite the particles of magnesium, is allowed to cool.

* Possibly in this case an unstable highly oxidised manganic compound may be at first formed, as in the case of chromium.

The metal may be purified by distilling it in a current of hydrogen. It is a silver-white metal, scarcely twice as heavy as water, and is to a certain extent malleable and ductile; the wire, however, is usually made by pressing strips of magnesium between fluted rollers, or by melting it in an apparatus not unlike a syringe, and forcing it out through a small hole by powerful pressure. It resembles zinc in many of its properties, melting at a point below redness, and volatilising at a higher temperature. It soon tarnishes in the air, but scarcely decomposes water at ordinary temperatures. When heated to redness in air or oxygen, it takes fire, and burns with a brilliant white light, forming white clouds of magnesian oxide. It will even decompose carbonic dioxide, as mentioned under that head. The light which it emits is very rich in chemical rays, and is now much employed for photography, a lamp being used in which a ribbon of magnesium is pushed forward through a tube at a fixed rate by clockwork, and ignited as it issues from the end of the tube. It has been proposed to employ it for general illuminating purposes, but there are difficulties in the way of producing a steady light which have not yet been overcome.

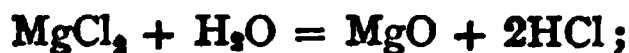
972. *Magnesian Oxide* (MgO) is the only known combination of oxygen and magnesium. It is the common 'calcined magnesia' of the shops, and is obtained by ignition of the carbonate, as in the case of lime. It is a soft, white, light powder, which unites with water to form a hydrate, and dissolves in it, but only to a very small extent, far less than even calcic hydrate. The solubility and alkalinity of magnesia are best observed by adding a spoonful or two of the powder to solution of reddened litmus, purple cabbage, or yellow turmeric. The colours of all of them will be changed in the way already so frequently mentioned. If the magnesia were not soluble, it could not produce these effects.

973. *Magnesian Carbonate* (MgCO_3).—This occurs in nature as the mineral magnesite, and is not easily procured artificially. What is sold as such in the shops ('magnesia alba') is prepared

by the addition of a hot solution of sodic carbonate to any soluble magnesian salt such as the sulphate. A white precipitate falls, which is a mixture of several magnesian hydric carbonates, and is not very definite in composition. From this compound most of the other magnesian salts may be obtained by dissolving it in the different acids.

974. *Magnesian Sulphate* ($\text{MgSO}_4, 7\text{H}_2\text{O}$).—This salt, often called Epsom salts, is prepared from bittern by evaporating it after the addition of hydric sulphate, or by the action of hydric sulphate on magnesian limestone. In the latter process, the resulting calcic and magnesian sulphates are separated from each other by digesting the mixture in a small volume of water, which takes up the readily soluble magnesian sulphate, and leaves the greater part of the calcic sulphate undissolved. Magnesian sulphate crystallises in rhombic prisms, which dissolve in 3 times their weight of water. The solution has a nauseous bitter taste, and is used in medicine as a purgative. Its ready solubility serves to distinguish it from the corresponding salts of barium, strontium, and calcium, as will be alluded to in describing the tests for the different metals.

975. *Magnesian Chloride* (MgCl_2) is obtained in solution by adding hydric chloride to magnesian carbonate. When the solution is evaporated to dryness, the chloride is decomposed by the last portions of water, thus:



and a residue of magnesia alone remains. If, however, it is previously mixed with excess of ammoniac chloride, a double salt is formed which can be evaporated without decomposition; and by further heating the ammoniac chloride, may be driven off, leaving pure anhydrous magnesian chloride.

976. When a magnesian salt is ignited on charcoal before the blow-pipe, a white infusible residue is left, which, when moistened with a drop of solution of cobaltous nitrate, and again ignited, becomes of a delicate pink colour. Magnesium compounds do not impart any colour to the blow-pipe flame, but

by passing a stream of electric sparks between wires of magnesium, the true spectrum of the metal may be obtained. It is found to contain lines which are coincident with certain solar lines (such as *b*, fig. 21), and we draw the same inference as in the case of barium, &c., that magnesium exists at the sun.

977. *Tests for Barium, Strontium, Calcium, and Magnesium.*—A solution of one salt of each of the four metals should be prepared, by dissolving in separate portions of 20 c.c. of water, 2 grms.* of baric chloride, strontic nitrate, calcic chloride, and magnesian sulphate, these being the salts most easily obtainable.

978. The first points to be observed are certain characters which distinguish the metals of this group from the alkalis on the one hand, and the remaining metals on the other.

(1.) To a portion of each of the four solutions contained in a test-tube, ammoniacal sulphide is added. It produces no precipitate. The only metallic salts in which this reagent produces no precipitate are salts of the alkalis and of the alkaline earths. Its negative action, therefore, shews us that we need not seek further for any of the other metals, but it leaves undetermined whether each glass contains the metal of an alkaline earth or of an alkali.

(2.) To determine this, fresh portions of the four solutions are taken, and to each a little ammonia and then some sodic phosphate are added. This produces in all of them white precipitates, consisting respectively of baric, strontic, and calcic phosphates, and magnesian ammoniacal phosphate. The salts of the alkali metals, it will be remembered, gave no precipitate with this reagent. This one test, therefore, distinguishes the whole group of metals we have just described from the whole of

* It is more strictly scientific to make solutions of the same chemical strength by dissolving in the same volume of water weights of the salts proportional to the weights of their molecules. Thus, we may conveniently take the weight of the molecule, expressed in grammes, and dissolve it in 2 litres of water. To take the case of barium: the molecular weight of baric chloride (BaCl_2) is 208, we should therefore dissolve 208 grms. of the salt in 2 litres of water, or 2 grms. in 20 c.c., and so on with the rest.

the alkali metals. In other words, a salt in solution which gives no precipitate with ammoniac sulphide, but does give a precipitate with sodic phosphate, ammonia having been previously added, must be a salt of barium, strontium, calcium, or magnesium. It remains, then, to discover which of these four metals is present.

(3.) Fresh portions of each of the four solutions are taken, and to each of them a saturated solution of calcic sulphate is added. It will immediately produce in the baric salt a white precipitate of baric sulphate. After some time, it will produce in the strontic salt a similar precipitate of strontic sulphate. But no precipitate will appear in the strontic or in the magnesian salt.

979. The cause of this difference is the relative solubility in water of the sulphates of this group. Baric sulphate is quite insoluble in water, and is therefore precipitated at once. Strontic sulphate has a certain solubility, and some time, accordingly, elapses before it shews itself. Calcic sulphate cannot produce a precipitate in a salt of calcium, because there is more than enough of water present to retain dissolved all the sulphate that can possibly be formed. Magnesian sulphate is greatly more soluble than calcic sulphate; so that if there be sufficient water present to prevent the latter precipitating, there must be enough to prevent the former.

980. A salt of barium, then, is distinguished from salts of the other metals of this group by being *immediately* precipitated by calcic sulphate; and as a confirmatory test, a little of the salt may be moistened with hydric chloride, and held on platinum-wire in the blow-pipe flame, when the green flame will be observed.

981. A salt of strontium is distinguished by being precipitated *after a short time* by the same sulphate. The dry salt may be further tested at the blow-pipe, or by kindling alcohol upon it, so as to see the crimson flame.

982. If a salt of an alkaline earth gives no precipitate with calcic sulphate, it must be a salt of calcium or of magnesium.

To discover which it is, some ammonia, and then a few drops of a solution of ammonic oxalate, are added to fresh portions of the two solutions. It will give a white precipitate immediately with the salt of calcium, but none with the salt of magnesium. The flame reaction may be applied, in confirmation, to the calcium salt; and in order to obtain a positive assurance that magnesium is present, a little of the dry salt may be heated on charcoal before the blow-pipe, and tested as described in par. 976.

ZINC.

| | Symbol. | Weight. | |
|-----------|---------|---------|----------------|
| Atom..... | Zn | 65 | Density = 7.1. |

983. *Occurrence.*—The chief ores of zinc are two: the carbonate (ZnCO_3), called calamine, and the sulphide (ZnS), called blende. Calamine was known to the ancient Greeks under the name of cadmia, as a mineral which, when fused with copper, imparted to it a bright yellow colour. In fact, although they did not isolate the metal itself, they made the alloy of it which we now call brass. Calamine is found in Siberia and Belgium, and also in Somersetshire and Derbyshire. Blende also occurs in crystallised masses in Derbyshire.

984. The metal is obtained from calamine by mixing the finely powdered mineral with coke or charcoal, and exposing it in peculiarly constructed crucibles to a red heat. The crucible has a hole pierced in the bottom, through which an iron tube passes, reaching nearly to the top of the crucible, while its lower end dips into a cistern of water. The crucible is provided with a tight-fitting cover. The reaction which takes place may be thus expressed:



The reduced metal, being volatile at the temperature employed, distils over, and is received in water. Zinc-blende is first roasted, that is, heated in a current of air, which burns away its sulphur, and the residue of zinc oxide which remains is treated in the same manner as calamine.

985. Zinc is a bluish-white metal, which slowly tarnishes in the air to a slight depth, in consequence of superficial oxidation, and is then protected by this film from further tarnishing. Its density is about 7.1. At ordinary temperatures, it is rather crystalline and brittle; but if heated to about 150° , it becomes quite malleable, and may be rolled out into sheets, as it now is extensively, being cheaper than lead and tin, for which it is substituted. Above this point it again becomes brittle, and may even be powdered in a mortar. At a full red heat (about 1040°) it rises in vapour, taking fire in open vessels, and exhibiting a rich green flame, somewhat resembling that of phosphorus when burning in a limited supply of air, but of a finer green. This appearance may be readily observed by heating zinc in a Hessian or fire-clay crucible in a common grate till the zinc begins to burn. It must be occasionally stirred, so as to secure the free admission of the air necessary for its combustion. The zinc, as it burns, is converted into a white flock-like substance, to which the alchemists gave the name of philosophers' wool. It is the zinc oxide carried up in the current of warm air.

986. Zinc is largely consumed, as a substitute for lead, in roofing houses, and instead of tin-plate for the construction of milk-pails and similar vessels. Another important use of zinc is in the manufacture of 'galvanised iron,' which is iron covered with a thin coating of zinc by immersing it, after being thoroughly cleaned, in a cistern of melted zinc. The two metals readily unite superficially, and the film of zinc protects the iron from injury by weather (par. 252, page 95). It is much employed, also, in the manufacture of galvanic batteries; and in combination with copper, as the important alloy brass, is of extensive application in the arts. It is interesting to the chemist as the ordinary source of hydrogen, which it furnishes when dissolved in most dilute acids. Its salts, also, are employed in the arts, and largely in medicine.

987. *Zinc Oxide* (ZnO).—Zinc forms but one oxide, closely resembling magnesia in appearance and properties. It is

prepared by burning the metal in air ; by heating the carbonate till the carbonic dioxide is expelled ; or by heating the hydrate (ZnH_2O_2) obtained by adding caustic potash to the solution of a salt of zinc, such as the sulphate. If excess of alkali be added, the zinc oxide, like alumina in similar circumstances, dissolves, forming a clear solution. When zinc oxide is exposed to a low red heat, it becomes yellow ; but when it cools to the ordinary temperature, it recovers its original white colour.

988. *Zinc Sulphate* ($\text{ZnSO}_4, 7\text{H}_2\text{O}$).—This salt, it will be remembered, was the residue of the process for hydrogen by the solution of zinc in diluted hydric sulphate. It crystallises in rhombic prisms, isomorphous with the crystals of magnesian sulphate. It is used in calico-printing, and in medicine as a lotion.

989. *Zinc Chloride* (ZnCl_2) is prepared most conveniently by dissolving zinc in hydrochloric acid. The metal combines with the chlorine, and hydrogen is evolved. The dry salt is highly deliquescent, and soluble in water and alcohol. An aqueous solution of it is extensively employed as an antiseptic and disinfectant. Wood saturated with it is said not to suffer from the dry-rot ; and it arrests the decay of animal matters, and decomposes offensive gases, such as hydric sulphide, so as to prove of service on board crowded ships, in hospitals, &c. It is also used by tinmen and braziers as a flux, for which purpose it seems to act by dissolving the thin film of oxide, which would otherwise prevent the close contact of the solder and the metal.

990. *Tests for Zinc*.—A solution of zinc sulphate is to be prepared, which must be free from iron. If it give a black precipitate with ammonium sulphide, and a brown one with caustic potash, iron is present. Most commercial specimens of zinc sulphate contain this impurity ; and if a pure specimen cannot be obtained, a solution must be prepared by dissolving zinc in diluted hydric sulphate.

991. Portions of the pure neutral solution of the zinc salt, placed in test-tubes, are examined as follows :

(1.) To the first, after addition of a few drops of hydric chloride, solution of hydric sulphide is added. It will produce no precipitate. This property is common to zinc, and all the metals of the analytical group to which it belongs. Its importance will appear hereafter.

(2.) To the second portion, ammonium sulphide is added. It produces a white precipitate of zinc sulphide, readily soluble in dilute hydric chloride.

(3.) To the third portion, caustic potash is added, drop by drop. The first additions of the alkali occasion a white precipitate of zinc oxide. The succeeding additions redissolve this, so that the liquid becomes clear again.

(4.) The second and third tests, it will be observed, produce the same effect upon a salt of zinc as they do upon one of aluminium. The potash solution from (3) is divided into two portions: to the one, solution of ammoniac chloride is added. It produces no precipitate. This proves the salt not to be one of aluminium. To the other portion, solution of hydric sulphide is added. It throws down a white precipitate of zinc sulphide. This proves the salt to be one of zinc.

992. There are, besides, two blow-pipe tests:

(1.) Zinc sulphate, or any other dry salt of the metal, is mixed in the state of powder with sodic carbonate, and heated on charcoal in the reducing flame of the blow-pipe. The charcoal becomes incrustated with a yellow powder, which changes to white when it cools. This appearance is owing to the production of zinc oxide, and is characteristic of the metal.

(2.) A more easily tried, and more striking blow-pipe test is to moisten a salt of zinc with solution of cobaltous nitrate, and heat it in the outer flame. It acquires a rich green colour.

CADMIUM.

| | Symbol. | Weight. | 1 litre of cadmium vapour weighs |
|---------------|---------|---------|-------------------------------------|
| Atom..... | Cd | 112 | 5.006 grms. |
| Molecule..... | Cd | 112 | Density of vapour (air = 1) = 3.94. |
| | | | " solid (water = 1) = 8.6. |

993. This metal closely resembles zinc in many respects. It is found associated with zinc in the ores of the latter metal, and, being the more volatile of the two, distils over with the first portions of metal in the process of zinc-smelting, already described. It is obtained pure by dissolving this alloy in hydric sulphate, passing hydric sulphide through the acid solution, which precipitates the cadmium alone, as sulphide. This sulphide, now free from zinc, is dissolved in boiling hydric chloride, and the cadmium precipitated as carbonate by the addition of sodic carbonate. The cadmic carbonate is then reduced by charcoal, in the manner described under ZINC.

994. Cadmium is a white metal, crystalline in structure, but moderately malleable and ductile. It fuses at 315° , and rises in vapour at about 450° . It forms alloys with various metals. When 'fusible metal' (see under BISMUTH) is melted with about one-tenth its weight of cadmium, an alloy is obtained which melts at the low temperature of 75° .

995. Cadmium is interesting as being one of the few metals the density of the vapour of which has been ascertained, and we have, therefore, some reliable evidence as to the composition of its molecule. A litre of its vapour weighs 5.0 grms. ; a litre of hydrogen weighs 0.0896 gm. ; and, according to the statement made in par. 380, page 145, we have the proportion :

$$0.0896 : 5 :: 2 : 112 \text{ (nearly).}$$

It is considered, then, that the molecule of cadmium weighs 112 times as much as the hydrogen atom ; and chemical reasons (such as the composition of the oxide, CdO) lead to the conclusion that the weight of the atom of cadmium is the same, and not, as usual, one half, or 56.

996. The compounds of cadmium are not very important. The iodide (CdI_2) and the bromide (CdBr_2) are used in photography, and the sulphide (CdS) is employed as a yellow paint, under the name of cadmium yellow.

997. The presence of cadmium in a solution may be recognised by the bright yellow precipitate formed on addition of hydric sulphide. This precipitate, which is cadmic sulphide, is insoluble in dilute hydric chloride, and also in ammoniac sulphide. Cadmium salts, when heated with sodic carbonate on charcoal before the blow-pipe, give off brown vapours of cadmic oxide (CdO), which form a very characteristic reddish-brown incrustation on the charcoal.

COPPER.

| | Symbol. | Weight. | |
|-----------|---------|---------|----------------|
| Atom..... | Cu | 63.5 | Density = 8.9. |

998. Copper is an abundant and valuable metal, and was known in very early times. It derives its name, through the Latin *cuprum*, from Cyprus, where rich deposits of its ores were found. It occurs in several forms.

(1.) Native, in a pure state, as fibrous and crystallised masses in veins of quartz-rock.

(2.) As sulphide, in copper pyrites, which is a combination of cuprous and ferric sulphides (CuFeS), and is found in large quantities in Cornwall, Cuba, and South America.

(3.) As carbonate, forming the beautifully veined mineral 'malachite,' the finest specimens of which come from Siberia. Great quantities are now imported from Chili and South Australia, and a blue variety, often crystallised, is found at Chessy near Lyons.

999. The greater part of the copper of commerce is smelted at Swansea, a locality possessing the advantages of a harbour and a cheap supply of coal from the adjacent Welsh coal-field. The smelting of copper ores, especially copper pyrites, is a very complicated series of processes, the chief difficulty being the removal of the iron present, which is effected by taking

advantage of the fact that copper has a greater affinity for sulphur and a less affinity for oxygen than iron. The ore (copper pyrites) is crushed to coarse powder, and calcined in a reverberatory furnace, fig. 75. This is a furnace with a low arched

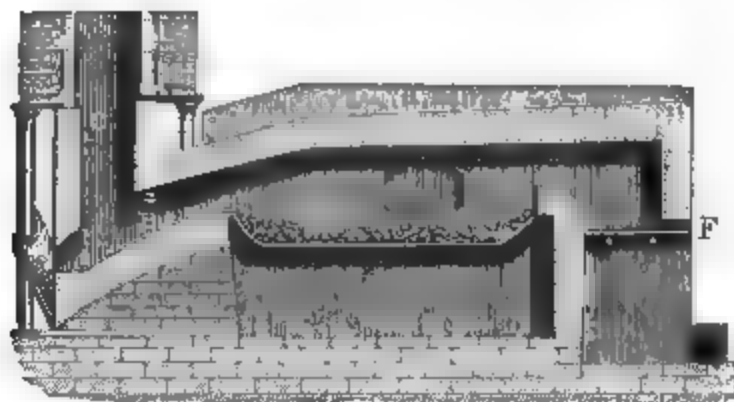


Fig. 75.

roof and a grate at one end, the ignited fuel being separated from the body of the furnace, A, by a low wall. By this construction the fuel never comes in contact with the substance to be heated, but the mass of flame and heated air is reverberated, or beaten back from the arched roof down upon the materials placed in A, and finally escapes up the chimney. By this treatment, the arsenic and part of the sulphur in the ore are oxidised and driven off in clouds of white smoke, which is highly suffocating and poisonous, and destroys the vegetation for several miles round Swansea.

1000. The calcined ore, which is a mixture of sulphides and oxides, is next transferred to another furnace, and heated more strongly, until it melts. The cupric oxide and iron sulphide act on each other, with formation of cuprous sulphide and iron oxide, the latter passing into the slag as silicate.

1001. By a repetition of these processes of calcination and melting, with addition of other ores such as the carbonate, a fused dark bluish-gray mass of nearly pure cuprous sulphide, called 'fine metal,' is obtained, and this is now reduced to metallic copper by a very interesting reaction, which is largely used in other smelting processes, such as that of lead. The

'fine metal' is once more calcined, with free access of air, until a certain portion of the sulphide is converted into oxide. The heat is then raised, and the oxide and the remaining sulphide act upon each other, forming sulphurous anhydride and metallic copper :



The crude product is cast into ingots, which are full of bubbles and blistered on the surface, owing to the evolved gases, and are known as 'blister copper.'

1002. The last process is that of 'refining.' The blister copper is brittle, and crystalline in structure, owing mainly to the presence of cuprous oxide. This is got rid of by melting the metal, covering its surface with charcoal, and thrusting into it a recently-cut branch of a growing tree. This is at once charred, and the gases evolved (chiefly hydro-carbons) agitate the whole mass, and quickly reduce the remaining portions of oxide. Samples of the metal are taken out at intervals, and tried by hammering out on an anvil. If they spread out into a plate without cracking at the edges, the proper point is reached, and the metal is ladled out into moulds. The operation of 'poling,' as it is called, may be continued too long, when the copper again becomes brittle, and is said to be 'over-poled.' The cause of this is not clear; it may be due to the presence of carbon (as in cast-iron) or of reduced antimony. The metal may be brought back to the malleable state by exposing it, while still melted, to a current of air for a short time.

1003. Copper is the only metal of a red colour. It is highly malleable and ductile, and an excellent conductor of heat and electricity. It is much used in the construction of electrical apparatus, such as galvanometers and induction coils, for which purposes it is drawn into wire no thicker than a fine hair. It melts at a bright red heat, but cannot be used for castings, since it contracts on cooling, and does not give a sharp impression of the mould: it is therefore chiefly wrought with the hammer.

1004. Copper forms many very useful alloys with other metals, of which the following may be mentioned :

(1.) *Brass*, which contains about 3 parts of copper and 1 of zinc, and is obtained by adding the proper proportion of zinc to melted copper, or (which is the ancient method) by strongly heating a mixture of calamine (see ZINC) and small fragments of copper. It has a well-known yellow colour, and is much harder and more readily filed and worked in the lathe than the tough fibrous copper itself. It may be hammered out into very thin leaves, which are used for cheap gilding, under the name of 'Dutch gold-leaf.' Muntz metal is a similar alloy, used for the sheathing of ships.

(2.) *German Silver*.—When a portion (about one-half) of the zinc in brass is replaced by nickel, a silver-white alloy is obtained, which is known by the above name. It is extensively used for making spoons, forks, &c., which are afterwards electroplated, or coated with silver.

(3.) *Bronze*.—This is an alloy of 90 parts of copper with 10 of tin, of a dull red colour, employed for guns, bearings of machinery, castings of statues, coinage, &c. It is remarkable that, when bronze is heated to redness and suddenly cooled, it becomes quite soft and easily worked in the lathe; but when very slowly cooled, it becomes hard and brittle. We shall see that with steel the case is exactly the reverse.

(4.) *Bell Metal*.—This contains more tin than bronze—about 20 per cent. It is rather brittle, and very compact and elastic in texture.

(5.) *Speculum Metal*.—This is also an alloy of copper and tin, containing an increased proportion of the latter (about 40 per cent.), together with a little arsenic. It is a brittle, brilliant-white alloy, which, from its hardness, takes an excellent polish.

1005. In moderately dry air, copper slowly acquires a brown tarnish, which is quite superficial, and is probably owing to the formation of a thin film of cuprous oxide (Cu_2O). In damp air, it acquires a green crust, from the formation of the

carbonate. When heated, however, nearly to redness in air or oxygen, it is readily oxidised, and two well-defined oxides, each the type of a series of salts, are known.

1006. *Cuprous Oxide* (Cu_2O).—In this compound, the copper appears to be monatomic, replacing hydrogen, atom for atom, in the molecule of water. It occurs native, in very perfect, ruby-red, semi-transparent crystals, belonging to the regular system. It may be obtained artificially by dissolving about equal weights of cupric sulphate and grape-sugar (or honey) in water, adding caustic potash to the solution until the precipitate at first formed (cupric hydrate) is re-dissolved, and boiling the liquid. The grape-sugar takes away oxygen from the salt, and a yellow precipitate of cuprous hydrate (CuHO) is formed, which, on further heating, turns red, owing to its decomposition into water and cuprous oxide.* The majority of the cuprous salts are colourless, and exceedingly prone, like most salts corresponding to the lowest oxides, to pass into higher salts. They may be obtained by acting upon cupric salts with metallic copper (just as the lower carbon oxide may be obtained by the action of carbon upon the higher oxide, par. 598, page 232). Thus, if the deep-blue solution obtained by adding excess of ammonia to a solution of cupric sulphate is digested for some time with copper filings or turnings in a closely stoppered bottle, it gradually becomes colourless; but when poured out into the air, it rapidly absorbs oxygen, and again becomes blue. Cuprous oxide, when heated with glass, gives it a beautiful ruby-red colour, which is, however, rather difficult to secure, owing to the readiness with which this oxide passes by absorption of oxygen into cupric oxide, which colours glass green.

1007. *Cupric Oxide* (CuO).—This is prepared:

- (1.) By heating sheet copper in a furnace to a red heat, with free exposure to air, till it becomes uniformly black.
- (2.) By raising cupric nitrate to a red heat in a crucible.
- (3.) By adding caustic potash to a solution of a cupric salt;

* This is a very delicate test for the detection of grape-sugar in presence of ordinary sugar, since the latter does not reduce cupric salts.

when a light-blue precipitate is formed, of cupric hydrate, which, when the liquid is raised to the boiling-point, loses water and becomes bark brown, being converted into anhydrous cupric oxide. This oxide is permanent at ordinary temperatures, but is readily reduced to metallic copper when heated with any substance capable of combining with oxygen. Thus, when a stream of dry hydrogen is passed over cupric oxide heated to redness in a bulb, *c*, fig. 76, water is formed, and condenses in the bottle, *d*, while metallic copper, in the form of a dull red powder, remains in the bulb. The same reduction occurs

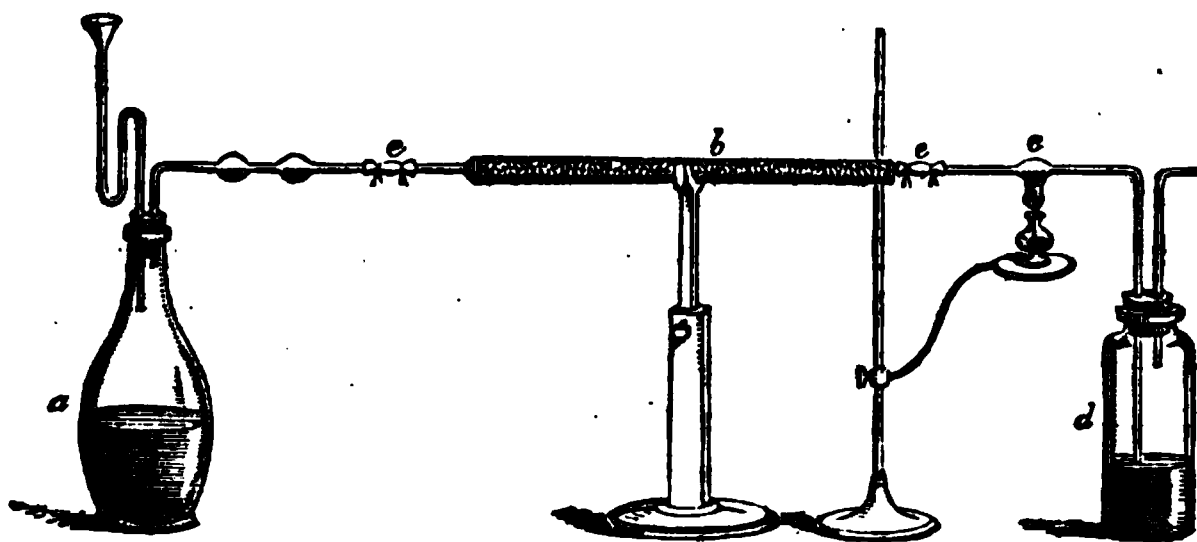


Fig. 76.

- a*, Flask for generating hydrogen.
- b*, Tube filled with fragments of calcic chloride to dry the gas.
- c*, Bulb of hard glass, half filled with cupric oxide.
- d*, Bottle to receive the condensed water.
- e, e*, Caoutchouc joints.

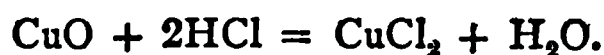
when cupric oxide is heated with organic substances; the carbon and hydrogen which they contain are oxidised to carbonic dioxide and water. This is the principle of the ordinary method of organic analysis. A known weight of the substance is intimately mixed with perfectly dry cupric oxide, placed in a tube similar to BB, fig. 50, page 195, and heated to redness. The water and carbonic dioxide are collected in weighed tubes, such as E, F, in the figure, and a stream of pure air or oxygen is finally passed through the apparatus by connecting G with a gas-holder, to sweep out the last traces of gas.

1008. Copper is scarcely acted upon by cold hydric sulphate, whether strong or dilute, but dissolves in the hot acid with evolution of sulphurous anhydride (see page 295). Hydric chloride also has very little action on copper, unless heated with the finely divided metal. Hydric nitrate, even when dilute, readily dissolves copper, nitric oxide being given off (see page 214). In all these cases a blue or green cupric salt is formed.

1009. *Cupric Sulphate* ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), commonly called 'blue vitriol,' is prepared on the large scale by roasting the native cupric sulphide, and washing the residue with water, or by dissolving the old copper sheathing of ships, after calcination in a furnace, in diluted hydric sulphate. It forms large blue crystals, belonging to the doubly oblique system, and twice as soluble in hot as in cold water. This is the most important salt of copper, and is employed in medicine, in dyeing, and in the preparation of pigments. It is also the salt generally used in electrotyping (page 96).

1010. *Cupric Nitrate*, $\text{Cu}(\text{NO}_3)_2$.—A deep-blue, crystalline, very deliquescent, and corrosive salt. Its chief employment is in the production of cupric oxide for use in organic analysis.

1011. *Cupric Chloride* (CuCl_2).—This is prepared by dissolving cupric oxide in hydric chloride :



It is soluble in alcohol, and the solution burns with a rich green flame, like that which hydric borate exhibits.

1012. *Tests for Copper*.—No metal is more easily detected in combination than copper. The tests are easily applied, and are almost all very delicate. A solution of cupric sulphate, containing 2.5 grms. of the salt in each 20 c.c., may be used, and separate portions tested as follows :

(1.) Hydric sulphide produces a black precipitate of cupric sulphide, insoluble in dilute hydric chloride, and also in ammoniac sulphide.

(2.) Potassic hydrate produces a bright blue precipitate of

cupric hydrate (CuH_2O_2), which becomes black when boiled with water (page 404).

(3.) Ammonia in small quantity produces a greenish-blue precipitate, which, when the alkali is added in greater abundance, is dissolved, forming an azure-blue solution.

(4.) Potassic ferrocyanide produces a reddish-brown precipitate of cupric ferrocyanide. This test is best observed with a dilute solution.

(5.) If a plate of clean iron or steel be immersed in a solution of the sulphate, or any other salt, of copper, it is almost immediately covered with a thin layer of metallic copper. This, of course, is the most decisive of all tests, as the metal itself is seen, and the peculiarity of its colour excludes the possibility of its being confounded with any other.

(6.) If any salt of copper be mixed with sodic carbonate, and heated on charcoal in the inner blow-pipe flame, grains of metallic copper are obtained, of its characteristic colour. When a compound of copper is heated in a borax bead, it gives in the oxidising flame a bluish-green bead, in the reducing flame a red opaque bead, if the copper is present in some quantity.

1013. A word must be said about the deep-blue compound formed in experiment (3), when ammonia in excess is added to a cupric salt. The solution yields crystals on evaporation, the constitution of which, after heating, may be expressed by the formula $(\text{H}_6\text{CuN}_2)\text{SO}_4$; the basic radicle being one in which part of the hydrogen in two molecules of ammonium (H_8N_2) is replaced by copper. Several of these 'cuprammonium' radicles are known, and afford good illustrations of replacement in molecules.

MERCURY.

| | Symbol. | Weight. | |
|---------------|---------|---------|---|
| Atom..... | Hg | 200 | 1 litre of vapour weighs 8.923 grms. Density of liquid = 13.6. |
| Molecule..... | Hg | 200 | |

1014. Mercury has been known from a very early period, and attracted much of the attention of the alchemists, who believed that gold and other metals were compounds of mercury with

sulphur in various proportions. The metal still retains its old alchemical name, 'mercury,' given to it on account of its mobility; and from the same property is derived the name 'quicksilver,' and the Latin, or rather, Greek word, *hydrargyrum* (water-silver), which has given rise to the symbol for its atom, Hg.

1015. Mercury is found native at Almaden in Spain, but its chief ore is its sulphide, the mineral 'cinnabar,' which occurs in Spain, Idria, and California. The process for obtaining it is very simple; the ore is crushed and roasted, either alone or with addition of quicklime, in cast-iron cylinders connected with a series of condensing chambers or earthen tubes. The sulphur combines with oxygen, forming sulphurous anhydride; while the mercury, having little affinity for oxygen at the high temperature employed, rises in vapour, and is readily condensed. It may be obtained nearly pure by a second distillation:



1016. The student may imitate the process on the small scale by mixing a little vermilion (which is chemically identical with cinnabar) with quicklime in a test-tube, and applying heat. The red colour will rapidly disappear, as the sulphur combines with the calcium of the lime, while calcium sulphide and sulphate are formed, and metallic mercury condenses in globules in the cool part of the tube.

1017. Mercury is a silvery-white metal, and is remarkable as being the only element except bromine which is liquid at ordinary temperatures. Its density at 0° is 13.59. It becomes solid at -39.4° , and contracts greatly as it solidifies, so that the density of frozen mercury is 14.0. In the solid state it is soft and malleable. It rises in vapour to a certain extent, even at ordinary temperatures, and dangerous accidents have occurred on board ships conveying it from South America, in consequence of the leakage of the iron bottles containing it, and the poisonous action of the mercurial vapour on the crew. It boils at 350° , being converted into a heavy invisible vapour, 1 litre

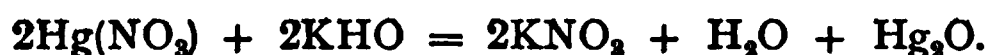
of which weighs 8.93 grms., which is 100 times the weight of a litre of hydrogen. It is extensively used in the extraction of silver from its ores, and in several silvering and gilding processes. In the laboratory it is of great value for various manipulations with gases, since comparatively few gases act upon it. It is used, moreover, in the construction of barometers and thermometers, for which latter purpose it is eminently adapted, from its low specific heat (par. 138), the regularity of its expansion by heat, and the great range of temperature between its freezing and boiling points.

1018. The alloys of mercury with other metals are called 'amalgams,' a name derived from *ἄμα, γαμίζω*, and occurring in the mystic language of the alchemists. An amalgam of tin, zinc, and mercury is placed upon the rubbers of electrical machines, to increase the development of electricity; and the reflecting surface at the back of ordinary looking-glasses is an amalgam of tin and mercury. The process of 'silvering' mirrors is as follows: A sheet of tin-foil is spread on a flat iron table; mercury is then poured over it, and the plate of glass is slid over the surface of the mercury so as to exclude air-bubbles. The glass is then pressed down by heavy weights, so as to squeeze out all superfluous mercury, and left for several days to allow the amalgam to form and consolidate.

1019. *Mercuric Oxide* (HgO).—Mercury does not become oxidised or tarnished in the air at ordinary temperatures, if pure; but when heated nearly to its boiling-point, it slowly combines with oxygen, and red scales form on its surface. These scales consist of mercuric oxide (HgO), the substance from which Priestley originally obtained oxygen, since at a higher temperature the oxide is decomposed, as already noticed (par. 13, page 5), into mercury and oxygen. Lavoisier, the great French chemist, determined the composition of air by this means: he heated mercury for some days in a known volume of air, and observed the diminution in bulk of the air; he then collected the mercuric oxide formed, and found that, when further heated, it gave off a volume of gas equal to the

amount absorbed from the air; and this gas he examined, and was the first to call oxygen. Mercuric oxide is usually prepared by gentle ignition of mercuric nitrate, as long as nitric peroxide is evolved. It then appears as an orange-red crystalline body, sometimes called 'red precipitate.' When procured by the addition of caustic potash or lime-water to a solution of mercuric chloride (corrosive sublimate), it appears as a yellow precipitate, and much paler in colour than the crystalline variety.

1020. *Mercurous Oxide* (Hg_2O).—This is prepared by adding caustic potash to a solution of mercurous nitrate:



It is a nearly black, heavy powder, readily decomposed either by heat or by the sun's rays into mercuric oxide and metallic mercury.

1021. The above oxides are representatives of the two classes of salts formed by mercury—namely:

(1.) Mercurous salts, such as mercurous chloride ($\text{Hg}'\text{Cl}$), in which mercury appears to be monatomic, and which are in several respects analogous to argentic salts.

(2.) Mercuric salts, such as mercuric chloride ($\text{Hg}''\text{Cl}_2$), in which mercury is diatomic, like barium, zinc, &c. This is the first instance we have had of a metal forming two distinct, moderately stable series of salts; and it will be well to consider what constitutes the difference between these series, and what is meant by the statement that a member of one series, a mercurous salt, passes by 'oxidation' into a member of the other series, a mercuric salt. The formulæ of a few of the salts are given below:

| | Mercurous Salts. | Mercuric Salts. |
|----------------|-------------------------|--------------------------------|
| Chloride | $\text{Hg}'\text{Cl}$ | $\text{Hg}''\text{Cl}_2$. |
| Nitrate..... | $\text{Hg}'\text{NO}_3$ | $\text{Hg}''(\text{NO}_3)_2$. |
| Oxide..... | $\text{Hg}'_2\text{O}$ | $\text{Hg}''\text{O}$. |

It is evident that, in passing from one series to the other, the mercury changes its atomicity, its power of saturation of the other radicle. Thus, in mercurous chloride, 200 parts of

mercury saturate 35.5 parts of chlorine; while, in mercuric chloride, the same weight of mercury saturates twice as much, or 71 parts of chlorine. The atomicity is generally determined by the presence of excess, or defect, of the radicle to be combined with the mercury. For instance, if mercury is acted on by a small proportion of chlorine, mercurous chloride is formed; if by excess of chlorine, mercuric chloride is obtained. Moreover, when mercurous chloride is treated with excess of chlorine, the mercuric salt is formed; and, by heating the latter salt with excess of mercury, it passes into the mercurous salt. Although, then, we may, by analogy, speak of the change as an oxidation, yet oxygen is by no means necessary to produce it. In a word, the term 'oxidation' is used to express a change in the composition of a salt analogous to that which occurs when a lower oxide passes into a higher oxide by absorption of oxygen.

1022. Mercury is quite unacted upon by hydric chloride, even when the concentrated and boiling acid is used. It is dissolved slowly by cold hydric nitrate, and rapidly by the hot acid. Hydric sulphate, when heated to boiling, dissolves the metal, as mentioned under the head of SULPHUROUS ANHYDRIDE. In each case, a mercurous or mercuric salt is formed, according to the proportions of the metal and acid, and the temperature.

1023. *Mercuric Chloride* (HgCl_2).—This salt, which is often known as 'corrosive sublimate,' is prepared by mixing mercuric sulphate with an equal weight of common salt, and applying heat to the mixture contained in a retort.



The mercuric chloride rises in vapour, and condenses as a crystalline sublimate. It fuses at 265° , and boils at 295° , and a litre of its vapour weighs 12.4 grms. It is soluble in water, alcohol, and ether. It is a deadly poison, and serious accidents have occurred from its substitution for calomel. It forms an insoluble compound with white of egg, which is administered

as an antidote to its poisonous effects. This property of coagulating various animal and vegetable matters, has led to the employment of corrosive sublimate for preventing the decay of timber, &c. In the process of 'kyanising' wood (so called from its inventor), a solution of corrosive sublimate is forced into the vessels of the timber, under pressure, when the sap is rendered insoluble, and putrefaction prevented.

1024. *Mercurous Chloride* (HgCl).—To prepare this salt, which is commonly called calomel, mercuric sulphate has as much metallic mercury as it contains already ground with it in a mortar. Common salt is then added, and the mixture is heated, as the materials for corrosive sublimate were. Calomel, which, as well as the higher chloride, is volatile, rises in vapour, and condenses in crystals. If mercurous sulphate could be prepared as readily as a mercuric sulphate can, it would be employed in the preparation of calomel. The mechanical mixture of mercury and the higher sulphate is equivalent to a mercurous salt, and acts as such when heated with common salt. The most convenient mode of procedure is to take any quantity of mercury, and divide it into halves by weight. The one half is converted into mercuric sulphate by boiling with hydric sulphate. It is then dried and triturated in a mortar with the other half of the mercury, and the resulting mixture is sublimed with an equal weight of salt. Calomel is also obtained by mixing solutions of common salt and mercurous nitrate, when it is precipitated as a white powder, being, unlike corrosive sublimate, quite insoluble in water. It volatilises, but without previous fusion, as readily as the higher chloride, and a litre of its vapour weighs 10.7 grms. It is much less poisonous than the higher chloride. The student should be careful, when preparing it or corrosive sublimate, to avoid inhaling the vapours of the volatilising salts, as salivation is readily induced by a small amount of either mercury chloride when it enters the body by the lungs.

1025. It is necessary also to point out that the names of calomel and corrosive sublimate in the pharmacopœia have

been frequently changed in consequence of alterations of opinion as to the atomic weight of mercury, some representing it, as is done in this book, as 200, others as one-half that number. If the atomic weight be made 100, calomel is the subchloride, and corrosive sublimate the protochloride. If 200, calomel becomes the protochloride, and corrosive sublimate the bichloride or perchloride. The protochloride of one person approving of the one atomic weight thus comes to be the perchloride of another employing a different equivalent—a circumstance which may lead to the most dangerous results when the chlorides of mercury are purchased for medicinal use, since the fraction of a grain of the higher chloride is a sufficient dose, and a patient who had corrosive sublimate given to him instead of calomel, would, in the majority of cases, receive a fatal dose. It is best, therefore, in writing prescriptions, to distinguish them by their trivial names of calomel and corrosive sublimate; but if it is deemed necessary to use chemical titles, it will be found safest to call calomel the *subchloride*, and corrosive sublimate the *perchloride*, although these are not according to strict theory.

1026. *Mercuric Iodide* (HgI_2).—This is prepared by mixing solutions of mercuric chloride and potassic iodide (par. 713 (4), pages 282–3):



The mercuric iodide is soluble in excess of either salt, and hence they should be taken exactly in the proportions indicated in the above equation. This substance, like many other mercury salts, exists in two allotropic forms. At the first moment of its precipitation it is yellow, but it rapidly changes to scarlet, and is, indeed, employed as a paint, being one of the purest scarlets which can be artificially produced. When this scarlet powder is dried and heated in a test-tube, it changes to yellow and sublimes, forming yellow prismatic crystals. These crystals very shortly turn scarlet—the change beginning at one point, and spreading through the whole mass. This change is produced immediately if the crystals are pressed

or rubbed, and may be strikingly shewn in the following way: A little of the scarlet iodide is placed on a plate, which is covered with a sheet of writing-paper, and placed in hot sand. An even layer of the yellow iodide is thus formed on the paper, and when letters are traced on this with a glass rod, they immediately appear in scarlet. This change of colour is accompanied by a change of crystalline form, the yellow prisms changing into an aggregate of red octahedra, as may be seen by watching the precipitation under the microscope.

1027. *Mercuric Sulphide* (HgS).—This is the valuable pigment vermilion, and, like the iodide, exists in two forms. It is usually prepared by grinding together mercury and sulphur, and slowly heating the mixture until it sublimes. It may also be obtained by the action of hydric sulphide in excess upon mercuric chloride, when it is precipitated as a black powder, which, when warmed for some time with solution of ammoniac sulphide, turns red, without change of composition.

1028. *Tests for Mercury*.—Salts of mercury may be identified by mixing them with anhydrous sodic carbonate, both substances being perfectly dry, and heating the mixture in a small tube sealed at one end, when a sublimate of small globules of mercury (easily seen under a lens) will be formed. Moreover, a piece of bright copper, introduced into a solution containing mercury, acidified with hydric chloride, is soon coated with metallic mercury, which becomes bright like silver when rubbed. These two tests are perfectly conclusive as to the presence of the metal, but give no indication whether a mercurous or mercuric salt is present.

1029. To observe the reactions of the mercurous salts, a solution of mercurous nitrate may be made by digesting about 3 grms. of mercury with 20 c.c. of slightly diluted hydric nitrate, until the metal is nearly all dissolved. Separate portions are to be tested as follows:

(1.) On addition of hydric chloride, a white precipitate of mercurous chloride is produced, which dissolves, owing to its conversion into mercuric chloride, when more hydric chloride,

together with a little hydric nitrate, is added, and the mixture warmed. It is turned black by ammonia.

(2.) On addition of hydric sulphide, a black precipitate of mercurous sulphide (Hg_2S) is formed, which is insoluble in hydric chloride and in ammoniac sulphide.

(3.) On addition of potassic hydrate, a black precipitate of mercurous oxide is formed.

1030. As an example of a mercuric salt, a solution of mercuric chloride containing 2.7 grms. of the salt in 20 c.c. may be used.

(1.) On addition of hydric chloride, no precipitate is formed.

(2.) On addition of hydric sulphide, drop by drop, to the acid solution obtained in experiment (1), a white precipitate is at first formed, which becomes yellow, then brown, and finally black, as more and more of the hydric sulphide is added. The ultimate product is mercuric sulphide.

(3.) Potassic hydrate gives a yellow precipitate.

(4.) Stannous (tin) chloride, added drop by drop, yields at first a white precipitate of mercurous chloride :



But if the reagent is added in excess, the colour of the precipitate changes to gray, owing to its reduction to metallic mercury. If this is allowed to subside, the solution poured off, and the precipitate boiled with a little more stannous chloride and hydric chloride, the scattered particles will unite into one globule of mercury.

1031. We have more complete evidence as to the weight of the atom and molecule of mercury than is usual among the metals. From its comparatively low boiling-point, its vapour-density has been determined pretty accurately by Dumas to be 6.97 (air = 1). Hence, a litre of air weighing 1.293 grm., a litre of mercury vapour will weigh ($1.293 \times 6.97 =$) 9.01 grms. Then, according to the ratio explained in par. 380, page 145 :

| Weight of 1 litre of Hydrogen. | Weight of 1 litre of Mercury. | Weight of molecule of Hydrogen. | Weight of molecule of Mercury. |
|-----------------------------------|----------------------------------|------------------------------------|-----------------------------------|
| 0.0896 | : 9.01 | :: 2 | : 201. |

1032. In the next place, the density of the vapour of mercuric chloride is found to be 9.6. One litre of it, therefore, weighs 12.4 grms., and this weight of the salt yields on analysis 3.2 grms. (equivalent to 1 litre) of chlorine, and 9.2 grms. (approximately 1 litre) of mercury. Now, since we are unable to take out the mercury from mercuric chloride except as a whole, we must conclude that only one atom is present in a molecule of the salt. Hence the mercury atom must weigh 201 times as much as the hydrogen atom. The analysis of other compounds confirms this result. For instance, the composition of mercuric oxide is :

| | |
|--------------|--------------|
| Mercury..... | 92.6 |
| Oxygen..... | 7.4 |
| | <u>100.0</u> |

Then, if we assume that its molecule contains one atom of mercury associated with one atom of oxygen :

| Weight of Oxygen. | Weight of Mercury. | Weight of Oxygen atom. | Weight of Mercury atom. |
|----------------------|-----------------------|---------------------------|----------------------------|
| 7.4 | : 92.6 | :: 16 | : 200.2. |

1033. Lastly, the specific heat of mercury is .033, and, according to the law given in par. 141, page 55, the atomic weight of mercury should be that number which, multiplied by .033, gives a product approximately equal to 6.4. Now, 200 multiplied by .033, gives the product 6.6, and thus we gain a further corroboration, on physical grounds, of the former results.

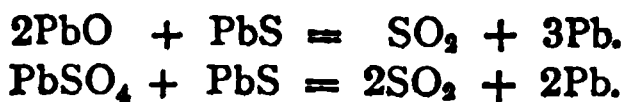
1034. It is to be noted that the numbers derived from the several lines of investigation are not absolutely concordant, but vary between 200 and 201. This is invariably the case in practice, owing to unavoidable errors of manipulation ; and the chemist always deduces his final result from a number of different investigations, being careful to assign the highest value to those modes of experimenting which have the fewest sources of error.

LEAD.

| | Symbol. | Weight. | |
|-----------|---------|---------|------------------|
| Atom..... | Pb | 207 | Density = 11.45. |

1035. Lead is another of the metals which were discovered and brought into use very early. It is mentioned in the Bible, and the Phoenicians are known to have traded in it from Britain. Remains of Roman lead-smelting works may even now be seen in Derbyshire and on the Mendips, and the heaps of slag near these works are being re-smelted as ores of lead by the improved modern processes. The Latin name for lead is *plumbum*, whence the symbol of its atom, Pb, is derived.

1036. The only important ore of lead is the sulphide, galena, which occurs, sometimes crystallised in cubes, in veins (usually in limestone), in England, Spain, and Saxony. It generally contains silver in small proportion. The process of reduction is simple in principle, but the ore has to undergo a tedious process of crushing and washing to free it from earthy impurities, which, being lighter than the mineral, are carried off by a stream of water. It is then roasted on the bed of a reverberatory furnace, until a great portion is converted into oxide and sulphate. The supply of air is checked at this point, and the heat raised; the undecomposed sulphide then acts upon the oxide and the sulphate, with formation of metallic lead and sulphurous anhydride:



A considerable amount of galena is also reduced in a blast-furnace, peat being usually the fuel employed. The excess of air driven in is sufficient to get rid of the sulphur as sulphurous anhydride, and to convert the carbon of the fuel into carbonic oxide, which, as in the case of iron, is the real reducing agent.

1037. The metal thus obtained is far from pure; it contains a variable amount of silver, as well as traces of other metals,

such as antimony, which render it hard and difficult to work. It is therefore refined by a process invented by Mr Pattinson, of Newcastle, which depends on the fact, that the alloy of silver and lead is more fusible than the pure metal. The crude lead is melted in a large iron pot, and allowed to cool slowly. As the cooling proceeds, nearly pure lead crystallises out before the rest has solidified, and is removed to another pot by a perforated ladle. The still liquid alloy is ladled out into a third pot, and the process is repeated two or three times, until pure lead is obtained on the one hand, and, on the other, an alloy containing 10 grms. of silver in the kilogramme. This latter is now ready for the process of cupellation, which has been described under SILVER.

1038. Lead is a bluish-white metal, so soft as to be easily scratched, even by the finger-nail, and to produce a mark when rubbed on paper. It is highly malleable, but not very ductile, and possesses very little elasticity or tenacity. Although the expression 'as heavy as lead' is almost proverbial, yet lead is far from being the heaviest of the metals, its density being 11.45. It melts at 330° , and, when strongly heated, rises in vapour. Much lead is lost from this cause in the smelting process; and various methods are employed to condense the fine particles of 'lead-fume' which pass into the furnace chimneys.

1039. The uses of lead are numerous. When rolled into sheets, it is employed for covering roofs, and lining gutters and cisterns. Lead pipes are used for conveying water, and are made by first casting a short, thick, hollow cylinder of the metal, and then passing it through a series of holes in a steel plate, gradually diminishing in size, until it is reduced (as in the process of wire-drawing) to the dimensions required. Lead forms several important alloys. Shot consist of lead alloyed with a little arsenic to render it harder, and are made by dropping the melted metal from a height of 30 or 40 metres into cold water. The drops, partly on account of the greater fluidity which the addition of arsenic causes, are found to be almost

perfectly spherical, and are separated by sieves into various sizes. Type-metal is an alloy of antimony and lead, and will be referred to under ANTIMONY. Plumbers' solder consists of lead alloyed with from one half to an equal weight of tin.

1040. Lead slowly tarnishes in air, and the film of oxide produced protects it from further change. In a state of fine division, however, such as may be obtained by igniting plumbic tartrate, it takes fire when brought in contact with air. Under the surface of water free from salts, such as rain or distilled water, it becomes rapidly converted into oxide, which, in part, dissolves in the water, and renders it poisonous, so that very soft waters cannot be conducted through lead pipes, or kept in leaden cisterns. If the water, however, contain (as spring, well, and river water generally does) sulphates and carbonates, then insoluble salts are formed, which incrust the lead, and prevent the water being contaminated. A minute quantity of saline matter is sufficient to prevent water becoming poisonous by contact with lead, although water which has been kept in a leaden cistern is seldom wholly free from lead.

1041. *Plumbic Oxide* (PbO), or *Litharge*.—Lead is converted into this oxide by exposing it, whilst melted, to a current of hot air (as in the process of cupellation); also by heating plumbic carbonate to low redness. When carefully prepared, and not allowed to fuse, it is of a pale yellow colour, and is named *massicot*; but, if raised to a red heat, it fuses, and crystallises, on cooling, of a brick-red colour. In this state it is called *litharge*. It is used in great quantities by painters, and in the preparation of 'boiled oils,' since linseed oil, when heated with it, dissolves a portion, and acquires the property of quickly drying and becoming hard, owing to absorption of oxygen. A mixture of organic salts of lead is formed, which is the basis of the lead-plaster and sticking-plaster of the surgeon.

1042. *Red Plumbic Oxide* (Pb_3O_4), or *Red Lead*.—This substance is prepared by heating finely ground massicot to low redness, whilst a current of air flows over its surface. The oxide then absorbs more oxygen, although (since the composition of

red lead is found to vary) it is doubtful whether a definite oxide is formed, having the above formula. It is more probably a mixture of plumbic oxide and peroxide ($2\text{PbO} + \text{PbO}_2$). Red lead is employed chiefly as a pigment, and also in the manufacture of flint-glass, on which it confers brilliancy and fusibility (see par. 834, page 335).

1043. *Plumbic Peroxide* (PbO_2) is obtained by the action of dilute hydric nitrate on red lead; when the latter is separated into plumbic oxide, which dissolves in the acid, and plumbic peroxide, which is left as an insoluble, purplish-brown powder. This substance, in common with other high oxides, is a powerful oxidising agent. It gives off oxygen when heated, and detonates when rubbed with phosphorus.

1044. *Plumbic Carbonate* (PbCO_3).—The pure salt occurs native as cerusite at Leadhills in Lanarkshire, and is sometimes worked as an ore of lead. The common white lead is a mixture of plumbic carbonate and hydrate, and is obtained by placing thin sheets of cast-lead over pots containing vinegar (impure hydric acetate), and imbedded in a sort of hot-bed made of fermenting tan (oak bark). The metal is soon wholly converted into a white mass, which is afterwards ground up with oil. The action is a peculiar one, a very little vinegar serving to convert a large quantity of lead into white lead. It appears that some plumbic acetate is first formed, which is decomposed by the moist carbonic dioxide evolved from the tan, with formation of plumbic carbonate and hydrate, while hydric acetate is set free to act upon another portion of lead. White lead is used not only as a white pigment, but is mixed with the majority of colours used in house-painting, with a view to confer upon them *body* or *opacity*. In virtue of this quality, which it possesses in a high degree, a thin layer of it suffices to conceal and cover a previous coating of paint. It has the great disadvantage, however, already referred to, of blackening by hydric sulphide. The carbonate may be prepared on the small scale by mixing solutions of sodic carbonate and lead acetate.

1045. *Plumbic Nitrate*, $\text{Pb}(\text{NO}_3)_2$.—This salt is readily

obtained by digesting lead, its protoxide, or its carbonate in hydric nitrate, and concentrating till crystals separate. It is interesting chiefly as the source of nitric peroxide, which it yields along with oxygen when heated.

1046. *Plumbic Acetate*, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.—This salt is referred to here although its acid radicle has not yet been described, because it is the salt of lead most easily procured, and, upon the whole, most suitable for exhibiting the tests of lead. It is prepared by dissolving litharge in vinegar, and receives its common name of 'sugar of lead,' from its intensely sweet taste, and also, perhaps, from its resemblance in appearance, as usually sold, to loaf-sugar. It is, like the other salts of lead, very poisonous.

1047. *Tests for Lead*.—A solution of plumbic acetate, containing about 4 grms. dissolved in 20 c.c. of rain or distilled water, may be taken, and separate portions examined as follows:

(1.) On addition of hydric chloride, a white crystalline precipitate of plumbic chloride is thrown down, which redissolves when 5 or 6 times its volume of water is added and the solution heated, but is partly reprecipitated as the liquid cools.

(2.) On addition of hydric sulphide, a black precipitate of plumbic sulphide is produced, insoluble in dilute hydric nitrate. It will be remembered that a piece of paper, moistened with plumbic acetate, was used as a test for hydric sulphide (par. 768, page 307).

(3.) Potassic hydrate, when added in small quantity, produces a white precipitate of plumbic hydrate (PbH_2O_2), which redissolves in excess.

(4.) Hydric sulphate gives a white precipitate of plumbic sulphate, which is nearly as insoluble in water as baric sulphate.

(5.) Potassic chromate produces a bright yellow precipitate of plumbic chromate (PbCrO_4). This substance is extensively used as a paint, under the name of chrome yellow.

(6.) Compounds of lead, when heated on charcoal with sodic carbonate before the blow-pipe flame, yield a malleable globule of metallic lead, while a yellow incrustation of oxide forms on the charcoal.

Section IV.—Triatomic Metals.

1048. The metals of the group which will next be described, namely, aluminium, chromium, iron, cobalt, nickel, manganese, are characterised by forming an oxide to which a formula is assigned corresponding to that of nitrous anhydride, N_2O_3 . This oxide is termed a sesquioxide (from the Latin *sesqui*-, once and a half), because for every atom of the metal there is one atom and a half (if we may say so) of oxygen present in the molecule. Thus the formula of aluminic oxide is Al_2O_3 . Similarly, they form well-defined combinations with chlorine, in which one atom of the metal is united with three atoms of chlorine—aluminic chloride, for instance, being represented by the formula, $AlCl_3$.*

ALUMINIUM, OR ALUMINUM.

| | | | |
|-----------|---------|---------|----------------|
| | Symbol. | Weight. | |
| Atom..... | Al | 27.5 | Density = 2.6. |

1049. Aluminium is almost as abundant an element as silicon and oxygen, in combination with which it chiefly occurs. The most familiar, perhaps, of its native compounds are felspar and mica, which are silicates of aluminium associated with other bases, and have been already mentioned under SILICON (page 334). These are both constituents of granite and of several other igneous rocks. Certain varieties of these, by exposure to the atmosphere, become completely disintegrated. It is chiefly the felspar which undergoes the change; and it appears to be owing to the action of rain-water charged with carbonic dioxide, by which the mineral is decomposed into soluble potassic salts, which pass into the soil, and aluminic silicate, which constitutes the different kinds of clay. By such a process of disintegration as we have described, the clays of

* It is true that the vapour density of the substance points to a formula Al_2Cl_6 ; but, on the other hand, an examination of some organic compounds containing the metal gives results which confirm the simpler formula.

our arable soils are produced. When it is pure, clay is quite white, as we see in the porcelain clay of Devonshire and Cornwall, which is derived from colourless felspar. More frequently clay is red, owing to the presence of oxide of iron; or black, from the diffusion through it of vegetable matter. Slate is similar in composition to clay, but has been hardened and laminated by heat and pressure.

1050. The metal aluminium is now made in considerable quantities by each of the two following processes, which depend on the displacement of the metal from its combinations by sodium.

(1.) The mineral Bauxite, found in France, which is a mixture of aluminic and ferric oxides, is ignited for some time with sodic carbonate, when a sodic aluminic hydrate (AlNa_3O_9 , 'aluminate of soda') is formed, which is dissolved out by water. To the liquid, hydric chloride is added, and the precipitate of aluminic hydrate (AlH_3O_3) which is produced, is dried, mixed with sodic chloride and charcoal, and heated to redness in a current of chlorine. By this means, a volatile aluminic sodic chloride (AlNaCl_4) is obtained, and this is mixed with some fluorspar (as a flux), and about one-fifth its weight of sodium in small lumps, and thrown upon the bed of a reverberatory furnace, previously heated. A strong action takes place, and the reduced aluminium, melted by the heat produced, collects at the bottom in the form of an ingot. The reaction is simple: the sodium unites with the chlorine, and sets free metallic aluminium:



(2.) Cryolite, a native aluminic sodic fluoride, which has been mentioned under FLUORINE, is ground to powder, and mixed with some sodic chloride and metallic sodium, and heated to redness in a crucible. The reaction is analogous to that just described, but the metal obtained is not so pure.

1051. The lustre of aluminium is white, with a bluish tinge resembling that of zinc, and is not liable to tarnish, even in moist air. It is malleable and ductile, and may be obtained

in very thin leaves. It is very light, the density being 2.6 (about one-third that of silver), so that even at its present price (5s. per ounce) it is considerably cheaper than silver. It possesses, from its compactness of structure, great sonorous properties, a bar of it ringing with a clear note when struck. Its conducting power for heat and electricity is about the same as that of silver. It melts rather more easily than silver, and shews little tendency to become oxidised, even when melted. From its many valuable qualities, aluminium would be extensively used if it could be obtained cheaply; at present, it is used for jewellery of various kinds, and in the construction of scientific apparatus. The golden-yellow alloy which it forms with copper, called 'aluminium bronze,' has many of the good qualities of the metal itself, and is rapidly coming into use.

1052. Aluminium is scarcely acted upon by hydric nitrate, even when concentrated and boiling. It is dissolved by moderately strong hydric sulphate, but most readily by hydric chloride, and also by solution of potassic hydrate, hydrogen being evolved. Only one series of salts of the metal is known, corresponding to the sesquioxide. We shall describe them in the order suggested by their mode of preparation.

1053. *Aluminic Sulphate*, $\text{Al}_2(\text{SO}_4)_3$.—When clay is boiled with strong hydric sulphate, it is decomposed, with separation of silicic hydrate, and aluminic sulphate, a highly soluble salt, is obtained. It is largely used in the manufacture of alum, and in dyeing and calico printing.

1054. *Aluminic Potassic Sulphate*, $\text{AlK}(\text{SO}_4)_2, 12\text{H}_2\text{O}$.—Aluminic sulphate forms a remarkable double salt with potassic sulphate, which is better known under the name of *common alum*. This valuable salt may be prepared by mixing solutions of potassic sulphate and aluminic sulphate, and allowing the liquid to evaporate spontaneously.



The alum separates in large regular crystals, which are modifications of the cube and octahedron. It is generally, however,

manufactured in another way. At Hurlet, near Glasgow, at Whitby in Yorkshire, and elsewhere, large beds of shale, or indurated clay, occur, associated with abundance of iron pyrites, ferric sulphide (FeS_2). The shale, or alum-schist, as it is called, is dug up, and broken into small pieces, which are piled in heaps, frequently wetted, and left exposed to the air. The pyrites rises in temperature as it absorbs oxygen, and is converted into a mixture of ferrous and aluminic sulphates. As soon as this change has occurred, water is poured upon the alum-schist. It forms a solution of both the sulphates, which is concentrated by evaporation, and set aside to crystallise. The ferrous sulphate, which is much less soluble than aluminic sulphate, separates first, and is in greater part removed in this way, being itself a valuable salt. Potassic chloride is then added to the solution. It decomposes the remaining ferrous sulphate, and forms ferrous chloride and potassic sulphate. The latter salt unites with the aluminic sulphate, and the double compound separates as alum, whilst the ferrous chloride, which is now the more soluble salt, remains in solution.

1055. Alum has a peculiar sour-sweet and astringent taste. It acts like a strong acid on litmus-paper, and evolves hydrogen when zinc is added to its solution. It is used to a considerable extent in medicine. It is largely employed in the preparation of leather, and still more abundantly in dyeing, and in the preparation of pigments. Its application to the two latter purposes depends upon its attraction for organic colouring matters, and its affinity for textile tissues. The former property may be observed by adding to a solution of colouring matter, such as madder, cochineal, or litmus, first alum, and then solution of ammonia, when a precipitate of aluminic hydrate will be produced, and will carry down the colouring matter combined with it. Such compounds are called lakes.

1056. The attraction of alumina for the fibre of cloth may be shewn by filtering aluminic acetate, or a solution of common alum which has been partially neutralised by sodic carbonate, through linen or cotton, when part of the alumina will be

abstracted by these tissues, and retained. Colours otherwise fugitive are thus fixed, the cloth to be dyed being first impregnated with alumina, by soaking it in either of the solutions above mentioned, and leaving it to dry in a warm place. When dry, it is boiled in a solution of the required colouring matter, when the alumina attaches itself to the fibre on the one hand, and the dye-stuff on the other, so that a coloured compound is produced, insoluble in water, and not destroyed by soap, &c. Patterns are produced by printing upon the calico with a solution of aluminic acetate, thickened with gum. It is then immersed in the dye-vat, and afterwards thoroughly washed in many changes of hot water. The colouring matter is washed away, except in those parts where the aluminic salt, or 'mordant,' as it is called, has been applied.

1057. Aluminic sulphate forms similar double salts with other monatomic sulphates, which are all classed under the general name of ALUMS. Ammonia alum, $\text{Al}(\text{H}_4\text{N})(\text{SO}_4)_2$, has of late come into extensive use instead of common alum, on account of its cheapness, the ammonia being obtained from the waste liquor of gas-works.

1058. *Aluminic Oxide* (Al_2O_3), or *Alumina*.—This substance occurs native, forming the mineral corundum, and the sapphire and ruby, which owe their colours to the presence of a trace of chromium. The more impure and coarsely crystallised varieties constitute the emery which is used for cutting and polishing substances. Alumina may be artificially prepared by adding to an aluminic salt (such as alum) solution of ammonia, as long as it occasions a precipitate. A voluminous, white, gelatinous substance is formed, consisting of aluminic hydrate (AlH_3O_3). In this state, after being gently dried, it is readily soluble in acids and in alkalies; but, if heated to whiteness, it gives off water, contracts greatly in bulk, and forms a white, soft powder, not at all gritty or soluble in alkalies, and scarcely acted on by acids. This is pure aluminic oxide, which may also be obtained by igniting ammonia alum or aluminic sulphate.

1059. Alumina, whether hydrated or anhydrous, is insoluble

in water, possesses no taste, and does not alter colouring matters. It is quite different, therefore, in properties from the alkaline earths, and is a much weaker base. In the anhydrous state it absorbs water with great readiness without combining with it, so that it adheres to the tongue, and is felt to parch it. Clay retains this property, and the ends of tobacco-pipes are glazed, to prevent adhesion to the lips or tongue. Its affinity for colouring matters has been mentioned above. Alumina is not fusible by a forge or furnace heat, but it melts before the oxyhydrogen blow-pipe into a clear globule, possessing great hardness.

1060. *Aluminic Chloride* (AlCl_3) is used in the process for obtaining the metal. It is obtained by passing perfectly dry chlorine over a mixture of alumina and charcoal heated to redness in a porcelain tube:



It forms a nearly colourless, crystalline sublimate, which is extremely deliquescent, fumes in the air, and volatilises below a red heat.

1061. *Aluminic Silicates*.—These occur in various minerals, such as felspar, as we have already illustrated. The most interesting bodies of this class, however, are the clays, which are very variable in constitution, so that no common formula can be given for them. Clay is an essential constituent of the important fabric pottery. Of this there may be said essentially to be but two kinds—earthenware and porcelain. Earthenware consists of clay, mixed with a certain amount of ground flints or of old pots, to prevent its contraction when burned, which, after being fashioned into vessels, and dried in the air, is exposed to a high temperature, in a peculiar furnace or kiln. In this state the burned clay forms a firm, solid, but brittle mass, called 'biscuit ware,' which is porous, and pervious to water. It is quite opaque, exhibits no traces of fusion, breaks with an earthy fracture, and gives out, when struck, a dull sound. Flower-pots, and porous cells for galvanic batteries,

are made in this way. Crucibles are made of an extremely infusible fire-clay, found beneath the coal strata, especially at Stourbridge in Worcestershire.

1062. To render earthenware fit to contain liquids, it is glazed: in other words, a fusible glass, composed of felspar and flint-glass, reduced to powder, is made into a cream with water, and spread thinly over its surface. The vessel is then returned to the kiln, and heated till this coating melts, and forms an insoluble glassy varnish, through which ordinary liquids cannot penetrate. Stoneware is glazed in a very simple way, by the process of 'salt-glazing,' which consists in throwing common salt into the kiln. This volatilises and is decomposed by the clay, a fusible sodic silicate being formed on the surface of the vessels.

1063. Porcelain, on the other hand, may be said to consist of clay and glass, the materials of which are ground to fine powder, and formed into a uniform paste with water. This paste is then dried till it resembles dough in consistence, and can then be formed into vessels. When these are heated in the kiln, the glassy element of the porcelain melts, and binds together its earthy constituent, at the same time rendering the whole mass more or less transparent, as wax does paper when melted into it, and then allowed to consolidate. Porcelain is distinguished from earthenware by being semi-transparent, by breaking with a glassy fracture, and by ringing like a metal when struck. Various substances are employed as the glassy constituent of porcelain. Powdered flints are almost invariably made use of. Felspar is also used, so are calcic phosphate (burned bones) and borax. Every celebrated pottery has its own recipe, and all the processes are kept very secret. Porcelain, like earthenware, requires to be glazed, to render it impervious to liquids. Unglazed earthenware is largely employed in the construction of water-bottles for hot climates, where it is an object that the water shall slowly percolate through the walls of the vessel, and, by evaporation from its outer surface, cool the liquid within. For a similar reason

flower-pots are left unglazed, and so are the porcelain cells of galvanic batteries.

1064. *Tests for Aluminic Salts.*—A solution of alum, saturated at ordinary temperatures, may be used for the following experiments :

(1.) Addition of hydric chloride, and then hydric sulphide, produces no precipitate.

(2.) Ammonic sulphide produces a white precipitate, which consists, however, of aluminic hydrate, and not sulphhydrate, since the latter is not formed in presence of water; hydric sulphide escaping as gas.

(3.) To a third portion is added solution of caustic potash, drop by drop. The first few drops cause a precipitate of aluminic hydrate, but when more of the potash is added, the precipitate re-dissolves, and the liquid becomes quite clear.

(4.) This clear liquid is divided into two portions. To one of them, solution of hydric sulphide is added; it will produce no precipitate. To the other, solution of ammonic chloride is added in excess; a precipitate of aluminic hydrate will be again formed. Small quantities of aluminic salts may be detected in this way, if sufficient ammonic chloride (an equal volume) be added, and the liquid heated. Care must be taken, however, to test the potassic hydrate previously for aluminium, which it generally contains. Silicates also interfere with the reaction. These tests distinguish salts of alumina from all other compounds, those of zinc included.

(5.) There is, in addition, however, a striking blow-pipe test. If a salt of aluminium be heated on charcoal, at the outer blow-pipe flame, after being moistened with solution of cobalt nitrate, it will acquire a splendid blue colour.

CHROMIUM.

| | Symbol. | Weight. | |
|-----------|---------|---------|--------------|
| Atom..... | Cr | 52.5 | Density = 7. |

1065. Chromium is an interesting metal, from the variety and beauty of the colours of its compounds, which are largely

used by the painter and dyer. It receives its name from the Greek *χρῶμα* (chroma), colour. It belongs to the same natural group as aluminium, but forms a more extended series of compounds with oxygen, occurring in some cases as an electro-negative radicle, analogous to sulphur.

1066. The different compounds of chromium are procured from a mineral called *chrome iron ore*, which can be readily procured from any dealer in minerals. Its composition is expressed by the formula $\text{FeO} + \text{Cr}_2\text{O}_3$. A portion of this is to be ground to powder, and heated in a crucible with a mixture of potassic carbonate and nitrate. The oxygen of the nitre combines with both the metallic oxides, with formation of a mixture of ferric oxide (Fe_2O_3) and potassic chromate, a lemon-yellow salt which is dissolved when water is digested on the contents of the crucible, and may be obtained pure by crystallisation. It is, however, in general, converted into potassic dichromate (see par. 1071) by addition of hydric sulphate, before crystallisation, and this latter salt, which forms orange-red crystals, is the one usually met with in commerce.

1067. The metal chromium is but little known. It has been obtained, by the decomposition of chromic chloride by sodium or zinc, as a fine powder or in small crystals extremely hard and infusible.

1068. *Chromic Anhydride* (CrO_3).—This is the highest well-defined oxide of chromium. It is obtained by mixing a cold saturated solution of potassic dichromate with $1\frac{1}{2}$ time its volume of strong hydric sulphate:



Much heat is evolved, and the chromic anhydride separates in beautiful crimson needles as the liquid cools. It is very deliquescent, and dissolves in a small quantity of water, forming hydric chromate (H_2CrO_4). This, as well as the anhydride, is a very powerful oxidising agent, and cannot be brought in contact with organic matter without change, owing to the readiness with which the latter deprives it of half its oxygen. It

bleaches vegetable colours, and is employed to bleach palm-oil, preparatory to its conversion into soap. A solution of it in hydric sulphate is sometimes used instead of hydric nitrate in Grove's battery.* The following experiments will serve to illustrate its oxidising powers.

(1.) If a little chromic anhydride is heated in a tube, it melts and decomposes, giving off oxygen, and leaving a green mass of chromic oxide :



(2.) If a few drops of strong alcohol are poured upon some of the substance placed on a plate, a violent action occurs, often sufficient to set fire to the alcohol, hydric acetate is formed, and green chromic oxide is left.

1069. Hydric chromate is the type of a series of salts called CHROMATES, the analogy of which to the sulphates, indicated by their formulæ (H_2CrO_4 with H_2SO_4), is borne out in several other points, such as isomorphism, solubility, &c. They are all coloured salts, and several are of great value as pigments.

1070. *Potassic Chromate* (K_2CrO_4).—The preparation of this salt from chrome iron-stone has been mentioned already. It crystallises in short prisms, of a light yellow colour, isomorphous with potassic sulphate. When a solution of it is mixed with a little dilute hydric sulphate, the colour changes from yellow to red, owing to formation of a remarkable salt, potassic dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$):



1071. *Potassic Dichromate* seems to be analogous in constitution to 'Nordhausen acid' ($\text{H}_2\text{S}_2\text{O}_7$, par. 750, page 299) and to sodic diborate; the molecule may be represented to consist of neutral chromate associated with a molecule of chromic anhydride ($\text{K}_2\text{CrO}_4 + \text{CrO}_3$). It crystallises in fine red tables,

* A similar solution is the liquid used in the 'bichromate battery,' a most convenient form for purposes where great intensity without much constancy of action is required. It consists of a plate of amalgamated zinc and a plate of artificial graphite immersed in a saturated solution of potassic dichromate, to which $\frac{1}{4}$ th its volume of hydric sulphate is added.

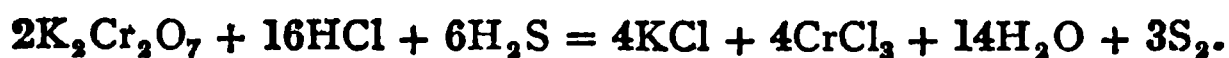
or short prisms, which may be readily obtained in the shops. A solution of potassic dichromate saturated in the cold, may be taken for the following experiments, which will serve to shew the properties and uses of the chromates :

(1.) On addition of solution of plumbic acetate, a bright yellow precipitate of plumbic chromate is formed, which (as already mentioned under LEAD) is used in painting and dyeing. When this substance is boiled with lime-water, or fused with nitre, a basic chromate (Pb_2CrO_5) is obtained of a beautiful vermilion-red colour.

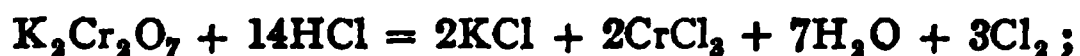
(2.) Solution of argentic nitrate gives a dull red precipitate, which, when crystallised from its solution in dilute hydric nitrate, is of a splendid ruby-red colour.

(3.) If paper, soaked in the solution of potassic dichromate, is exposed to light, a part being protected as described in speaking of photography (par. 933, page 375), the exposed portions gradually darken in colour, owing to some molecular change in the salt, by which it is rendered insoluble ; and when the paper is thoroughly washed in water, a reddish picture on a white ground is left. This is the basis of several photographic printing methods, such as the carbon, the autotype, and the heliotype processes, in which a film of gelatine containing potassic dichromate forms the sensitive surface.

(4.) When solution of hydric sulphide is added to a portion rendered acid by hydric chloride, a pale yellow precipitate of sulphur is formed, while the colour of the solution changes from red to green, owing to the formation of a chromium salt :



(5.) When a little alcohol is added to another acidified portion of the solution, and the mixture heated, a similar reduction of the chromate occurs, the solution turning dark green, and giving off pungent vapours of aldehyd, a substance obtained by the oxidation of alcohol. The same change may be effected by strong hydric chloride alone, chlorine being evolved :



and this process is sometimes used for the preparation of chlorine.

(6.) The two preceding experiments have shewn that a chromate readily gives up the oxygen it contains. But there are also indications that chromic anhydride will absorb more oxygen, forming a higher, very unstable oxide, of which the formula is uncertain. Thus, when a strongly acid solution of potassic dichromate is mixed with hydric peroxide (par. 968, page 388), an intensely deep-blue liquid is obtained, which almost immediately decomposes, giving off oxygen, and becoming green. If some ether is previously added, the blue substance dissolves in the ether, and its decomposition takes place much more slowly; but it has never been obtained in a pure condition. It would seem to be a high chromium oxide (possibly CrO_6), passing at once (or at least without our being able to arrest its decomposition at intermediate stages), by loss of oxygen, to the condition of chromic oxide, Cr_2O_3 .

1072. *Tests for Chromates.*—Chromates may be readily detected in solution by the reactions (1), (2), and (4) above given. An insoluble compound should be fused with nitre, and the potassic chromate formed may be detected in the usual way.

1073. *Chromic Oxide* (Cr_2O_3).—Several modes of forming this oxide have been already given. It is usually obtained from potassic dichromate by heating it in a crucible, either alone or mixed with sulphur, to a full red heat, and afterwards washing the contents of the crucible with water, and drying the residue. It is a dark green crystalline powder, insoluble in acids, and forms a very permanent paint called 'chrome-green.' It is also used in enamel painting, and in glass-staining, as it imparts to glass a fine green colour. It is a member of a series of salts called chromic salts, which are generally obtained by reduction of a chromate by one of the methods already mentioned. Chromic sulphate, $\text{Cr}_2(\text{SO}_4)_3$, forms with potassic sulphate, a double salt, called 'chrome-alum,' crystallising in violet octahedra, and analogous in many respects to common alum. The student may take a solution of this salt, or the solution of

chromic chloride obtained in expt. (5), par. 1071, to observe the reactions of chromic salts.

1074. (1.) On addition of ammoniac sulphide to a solution of a chromic salt, a bulky greenish precipitate of chromic hydrate (CrH_3O_3) is formed, and hydric sulphide evolved. (Compare the reaction of an aluminic salt, par. 1064, page 428.)

(2.) Potassic hydrate produces a similar precipitate of the hydrate, which readily re-dissolves in excess, forming a green liquid from which chromic hydrate is re-precipitated on boiling for a short time. Chromic hydrate is readily soluble in acids, and many chromic salts are thus prepared, but when it is heated to low redness, it contracts in bulk, and becomes anhydrous and insoluble.

(3.) If a chromic salt is fused with nitre, potassic chromate is formed of a bright yellow colour, the presence of which may be recognised in the usual way.

1075. All chromium compounds, when fused in a borax bead, impart a bright green colour to the bead, which is unaltered in the reducing flame.

1076. *Chromic Chloride* (CrCl_3) is obtained in beautiful violet crystals by passing dry chlorine over a mixture of chromic oxide and charcoal heated to redness. When hydrogen is led over this chloride heated in a tube, a portion of the chlorine is withdrawn, and a chromous chloride (CrCl_2), corresponding to a lower oxide (CrO), is formed.

1077. *Chromic Oxychloride* (CrO_2Cl_2).—This interesting compound is made by mixing equal weights of potassic dichromate and sodic chloride, and heating the mixture with excess of strong hydric sulphate in a glass retort, provided with a receiver. The substance rises as a deep red vapour somewhat resembling nitric peroxide, but redder in colour, and condenses into a heavy liquid-like bromine in appearance. Its vapour is even more irritating to the lungs than chlorine, and excites violent coughing. If dropped upon sulphur or alcohol it sets them on fire. It is at once decomposed by water, forming hydric chromate and hydric chloride.

IRON.

| Atom..... | Symbol. | Weight. | |
|-----------|---------|---------|----------------|
|Fe | | 56 | Density = 7.8. |

1078. Iron is, from its abundance and the combination of useful qualities found in it, the most valuable metal of all. It was not, however, discovered and worked at so early a period as copper. The 'bronze age' preceded the period in which implements of iron were made and used, since the smelting and manufacture of iron demanded a metallurgical skill, and a command of high temperatures, which was only acquired by long experience. The earliest mention of it in the book of Genesis informs us that Tubal Cain was 'instructor of every artificer in brass *and iron*;' and the ancient Egyptians appear to have been well acquainted with its uses for tools and weapons. Yet, in the Trojan war, the chiefs are represented by Homer as using bronze armour and weapons, and a ball of cast-iron was given as a most valuable prize at the funeral games described in the *Iliad*. The discovery of steel, and its property of becoming hard when quickly cooled, must have been made early, since ordinary iron would be unfit for the edge-tools mentioned in the Bible and in Homer. The Latin name for iron is *ferrum*, from which the symbol for its atom, Fe, and a nomenclature for its compounds, are derived.

1079. *Occurrence*.—Iron is found native, but only in very small quantities. It also occurs so pure as to be malleable in those remarkable bodies, meteoric stones, in association with nickel and other metals. Several enormous masses of meteoric iron have been discovered; one, in South America, was estimated to weigh 12 or 13 tons. In the state of vapour, it has been shewn by the spectroscope to exist at the sun, the line G, fig. 21, being, among many others, due to the presence of iron in the solar atmosphere. The practical sources of the metal, however, are its native oxides and carbonate, which form its most abundant ores.

(1.) Magnetic iron ore, or the black oxide (Fe_3O_4), is abundant in various parts of the world, especially Sweden and North America. It is the only iron oxide which is attracted by the magnet, and is frequently itself permanently magnetic, as in the mineral called loadstone. It contains about 72 per cent. of iron, and is reduced to the metallic state by heating it in a small blast-furnace with charcoal. This is the process employed in Sweden and India, and the iron which it yields affords much finer steel than any other.

(2.) Red oxide (Fe_2O_3), or hæmatite, is found in Lancashire and Cumberland, and in Germany, often in large rounded masses, with a fibrous structure. A crystallised variety, called 'specular iron ore,' occurs in Elba. It is sometimes smelted alone, in the same way as the magnetic oxide, but is generally mixed with less rich ores.

(3.) Ferrous carbonate (FeCO_3), or clay iron-stone, is the most abundant and important of the ores of iron. It is usually associated with clay and other silicates, and occurs in Staffordshire and South Wales, alternating with beds of coal and limestone, which are the very substances required for smelting it. A variety of it, called 'black band,' is found in Scotland and Lancashire. This ore contains on an average about 30 per cent. of iron, and requires a much more complex process for its reduction than the native oxides.

(4.) Ferric sulphide (FeS_2), or iron pyrites. This, although very abundant, is used chiefly as a source of sulphur, as already mentioned, since it does not yield a pure iron by any of the processes in use.

1080. *Iron-smelting processes.*—The greater part of the iron in commerce is obtained from clay iron-stone, by the use of the hot-blast furnace. The ore is first broken up and roasted or calcined, during which process it parts with any water it may contain, and with carbonic dioxide and coaly matter. The roasted ore is then introduced into a blast-furnace (fig. 77), which resembles in construction a conical or domed chimney, fifteen or twenty metres in height, and about four or five metres

in diameter within at the widest part. The ore and the materials required for its reduction are introduced by the top; and a high

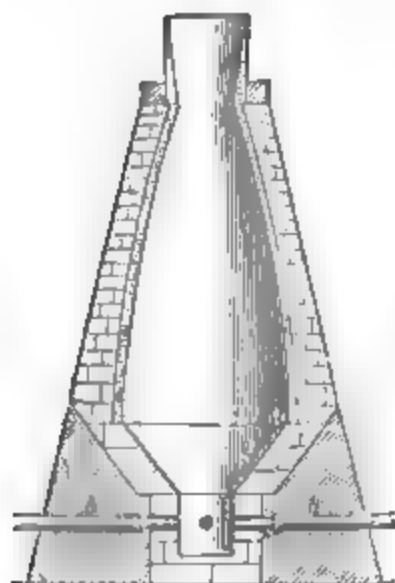
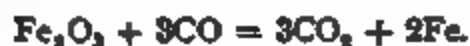


Fig. 77.

temperature is maintained by forcing in air through pipes (*b, b*) near the bottom of the furnace, through the medium of powerful blowing-machines. At one time, cold air was employed for this purpose, and the furnace was fed with coke; but within the last forty years an immense improvement has been effected by heating the air before it is driven into the furnace. The air is raised in temperature by being made to traverse a series of tubes heated by a fire, and arranged between the blowing apparatus and the furnace. It is thus heated to

between 300° and 400° , which is found the most suitable temperature. This is called the *hot blast*. It enables the iron-master to substitute raw coal for coke, and effects a saving of more than three-fourths of the coal which was requisite when the cold blast was employed.

1081. The roasted ore is mixed with a due proportion of limestone, and introduced into the furnace in alternate layers with coal. As the mass sinks down, more ore and fuel are added, and thus a furnace is kept uninterruptedly at work for years. The chemical changes may be traced as follows: When the air comes in contact with the coal, a vivid combustion ensues, and the carbonic dioxide produced, passing upwards, combines with more carbon from the fuel, forming carbonic oxide. This reduces the ferric oxide of the ore, forming metallic iron and carbonic dioxide:



The carbonic dioxide is again reduced by the fuel to carbonic oxide, and this acts upon more ferric oxide, and thus the

changes are repeated. The reduction of the iron is also aided by the hydrocarbons formed during the combustion of the fuel, and the mass gradually sinks to the hottest parts of the furnace, where the metal combines with a portion of carbon, forming a fusible carbide, which accumulates at the bottom of the furnace in a liquid state. Meanwhile, the lime and clay unite to form a fusible calcic aluminic silicate which floats upon the melted metal. These liquids are drawn off at intervals by different apertures: the former, when it consolidates, forms the slag of the furnaces; the metal is run into channels of sand, and constitutes the cast-iron, or pig-iron of commerce.

1082. Cast-iron, it will be observed, is not pure iron, but a compound of the metal with carbon. The latter occurs in it to the extent of five per cent. or more, which is nearly one atom of carbon to four of iron. Besides carbon, however, some silicon, derived from the clay, as well as manganese, and perhaps also calcium, magnesium, and aluminum, are present in small quantity in cast-iron. It is possible also that the rare metal titanium is present. Crystals of a compound of titanium are very frequently found imbedded in the slags within the blast-furnaces, when any circumstance leads to these being blown out.

1083. Cast-iron differs from malleable iron in being much more fusible, in possessing a highly crystalline structure, and in being greatly more brittle. Liquid cast-iron expands in becoming solid, and in consequence takes very sharp impressions from a mould, its increase in bulk causing it to insinuate itself into the finest lines, and so to present a faithful copy of each. This fact is not to be confounded with another, which has led to its being denied—namely, that an iron casting is always smaller than the wooden fac-simile, or original, from which its mould was made. This diminution of size is owing to the contraction of the iron *after* it has consolidated. It has swelled up into every crevice of the mould, however, before contraction commences. Two varieties of cast-iron may be distinguished:

(1.) *Gray Cast-iron* is comparatively fusible and easily filed

and turned, often coarse grained, with disseminated particles of graphite.

(2.) *White or Refined Cast-iron*.—This is obtained by exposing gray cast-iron in a melted state to a current of air. The impurities, such as silicon and carbon, are oxidised more readily than the metal itself, and a tin-white, hard, crystalline product is obtained, in which no uncombined carbon occurs.

1084. Malleable iron is prepared in this country from cast-iron by depriving the latter of carbon. The process by which this is done is called *puddling*. This is effected in a reverberatory furnace, see fig. 75, page 400. The cast-iron is laid in the bed of the furnace, where it speedily melts, and becomes partially oxidised at the surface. The workman then, by means of a long iron rod, or large oar-like spatula, puddles the melted metal—that is, stirs it up, so as to bring each portion of it successively to the surface. The object of the whole process is to convert the carbon of the cast-iron into carbonic oxide, and as the removal of the carbon proceeds, jets of that gas are seen burning on the surface of the metal with its characteristic blue flame. Water is sometimes sprinkled on the melted mass, or oxide of iron (hæmatite) or of manganese is added to supply oxygen more speedily to the carbon.

1085. One marked effect of the withdrawal of the carbon from the cast-iron is the diminution of its fusibility, so that although the temperature of the furnace remains unaltered, the metal ceases to be liquid, and becomes first pasty, and then, as the stirring or puddling is continued, granular—that is, like coarse-grained sand. The temperature of the furnace is now rapidly raised, till the sand-like particles of metal begin to grow pasty, and to agglutinate, a property of iron referred to already under welding. The workman, then, with his puddling-rod gathers together the particles of iron into large balls, which are removed from the furnace, and exposed on suitable anvils to large tilting or steam hammers driven by machinery. These squeeze out of the balls, as from a sponge, any portion of the cast-iron and ferric silicate still liquid within them, and at the

same time weld the particles of iron together into one solid coherent mass. The block of iron thus procured is heated a second time, and passed between large iron rollers, furnished with grooves, which convert the mass into a long rod or bar. Iron which is to sustain a great strain, such as that for anchor shanks, or the axles of railway carriages, undergoes this process several times, the long bar being cut into several short ones, which are tied side by side with iron wire, raised to a high red-heat, forged on the anvil, and passed between the grooved rollers again and again. Great tenacity is thus given to the metal.

1086. The bar or malleable iron thus procured is not crystalline in structure, or nearly so brittle as cast-iron. Its texture is fibrous, which is well seen by immersing a wire in a dilute acid, and allowing the latter to act till it dissolves to some slight depth the outer surface. The toughness and fibrous character of malleable iron slowly disappear if it be exposed to continued violent concussion, in consequence, as is believed, of the development of a crystalline structure, so far analogous to that which is always present in cast-iron. Several of the dangerous accidents on our railways which have resulted from the breaking of carriage axles, are referred to such a development of brittle crystalline structure in the iron of the axle, in consequence of the concussions to which it is exposed during the rapid motion of a railway train.

1087. The malleable iron of commerce is never quite free from carbon, and contains, in addition to about one-half per cent. of it, small quantities of silicon and the various metals present in cast-iron. The average composition of the different varieties of iron is given below.

| | Cast-Iron (melts at 1600°). Gray. White. | | Wrought-Iron (melts about 2000°). | Steel (melts about 1800°). |
|-----------------|---|-------------|--------------------------------------|-------------------------------|
| Iron..... | 92.3 | 97.8 | 99.4 | 98.0 |
| Carbon..... | 3.0 | 1.7 | 0.3 | 1.8 |
| Silicon | 4.3 | 0.3 | 0.1 | 0.1 |
| Phosphorus..... | 0.4 | 0.2 | 0.2 | 0.1 |
| | <hr/> 100.0 | <hr/> 100.0 | <hr/> 100.0 | <hr/> 100.0 |

1088. *Steel*.—Malleable iron is converted into steel by adding carbon to it, to a smaller extent, however, than it occurs in cast-iron. Only the purest iron, reduced from its native oxides, is employed for this purpose, and the process is called cementation. Bars of this iron are placed in alternate layers with charcoal powder in iron boxes, and the whole exposed to a high red-heat for forty or fifty hours. At the end of that period, the iron, without having undergone fusion, is found to have combined with about one and a-half per cent. of carbon, and to have lost its fibrous texture, having become hard and close-grained. The carbon has thoroughly penetrated the iron, being probably transferred from particle to particle, by the alternate formation and decomposition of a carbide. The surface of the bars is rough and blistered, and this form is known as blister-steel. For its finer applications, the bars of steel are welded together under the tilting-hammer, which gives the steel greater uniformity of composition and texture; and for the finest cutting instruments, it is melted, cast into ingots, and afterwards forged. It is then called cast-steel.

1089. Since steel is intermediate between cast and wrought iron, it would seem obvious that it might be formed by taking away a portion instead of the whole of the carbon from cast-iron. But in the first place, it is not easy to withdraw exactly the right proportion, and in the next place, unless the other impurities, such as the phosphorus and sulphur, are removed (as is done in the puddling process), the steel is of very inferior quality. These difficulties have, however, been overcome in a great measure by Mr Bessemer. His process consists in pouring melted cast-iron into large crucibles, and forcing a blast of air through it under high pressure from a pipe entering at the bottom of the crucible or 'converter.' The carbon is rapidly burnt off with evolution of intense heat, and the flame changing its appearance as the process continues, gives an indication of the time when the conversion is complete.* The current of

* One of the latest applications of the spectroscope has been in the examination of this flame in order to determine with precision when the proper point has been reached.

air is then stopped, a certain quantity of very pure cast-iron known to contain manganese is added, and the metal then poured into moulds. For this process, only those varieties of cast-iron which contain little or no sulphur and phosphorus are used, and the product is a very fair quality of steel, much cheaper than other kinds, and extensively used for boiler-plates, rails, axles, &c.

1090. Iron is often superficially converted into steel by the process of case-hardening. The finished articles are enclosed in a box with powdered charcoal (preferably animal charcoal), and heated to redness for two or three hours. The 'cementation' does not proceed far, but the layer of steel gives increased hardness and durability. The different parts of a gun-lock, for instance, are thus treated.

1091. Steel is much less fusible than cast-iron, but much more so than malleable iron. It is, on the other hand, inferior to the latter in malleability. Its most important character is the property it possesses of acquiring great hardness and brittleness, if raised to a high temperature, and then rapidly cooled, as by plunging it into oil or cold water. If, on the other hand, it be slowly cooled from a red heat, it becomes soft, like malleable iron, loses its brittleness and elasticity, and does not readily take or keep a sharp edge. By varying the temperature to which it is raised, after being hardened, it may be obtained of all degrees of hardness, from that given to files, which will scratch glass, down to that of a pallet-knife or spatula. Articles of steel are generally, after being forged, heated to redness and cooled quickly. They are then heated a second time to a temperature which is the higher the softer the steel is intended ultimately to be, and from this temperature they are permitted to cool slowly. This is called the *tempering* of steel. The temper of steel is usually judged of by observing the tint assumed by a bright surface of it when heated in the air, owing to the formation of a thin film of oxide, which gradually becomes thicker as the temperature rises. Thus at a temperature of 230° , the surface assumes a straw-yellow tint; the metal

has lost its extreme hardness, and is of the proper temper for razors. As the heat rises to 280° , the tint changes through dark-yellow to purple; the steel is now softer, and extremely elastic, and fit for swords, watch-springs, &c. At a still higher temperature, the colour becomes a uniform gray, and the metal is soft and annealed.

1092. Pure iron, which is very rarely seen, has, when polished, a white colour and brilliant lustre. Its specific gravity is between 7 and 8. It is a comparatively soft metal, and the most tenacious of all the metals. It is not a good conductor of heat or electricity; a fine iron wire becomes hot and melts when a strong electric current passes through it. A very remarkable property is its susceptibility of magnetism. When one pole of a magnet is brought near a bar of iron, the latter becomes magnetic, and will attract other pieces of iron. But this power wholly ceases, if the iron is pure, as soon as the magnet is withdrawn. Steel, on the contrary, retains this magnetism for a time varying with its quality and hardness. If a straight piece of watch-spring, or a long needle, is laid on a table, and the north pole of a magnet passed, with some pressure, from the centre to one end, and then the south pole from the centre to the other end, the steel becomes a permanent magnet, attracting small nails, and placing itself north and south when suspended by a thread. The harder the steel is, the more difficult it is to magnetise it, but the longer it retains its magnetism. Iron forms scarcely any alloys of importance. The ordinary 'tin-plate' consists of sheets of iron covered with a thin film of tin, by a process similar to that for galvanising iron (par. 986, page 395).

1093. Iron does not become oxidised, or rust, in perfectly dry air, but in moist air, or under water, it is rapidly converted into oxide, especially in presence of carbonic dioxide. At a red heat it unites readily with oxygen, even decomposing water, as already mentioned, par. 466, page 179. It is attacked rapidly by almost all acids, usually with evolution of the displaced hydrogen. There is one point in its behaviour with

hydric nitrate which deserves notice. If a piece of iron is dipped into the strongest hydric nitrate, an action begins, but almost immediately stops entirely, and the metal may now be placed in a more dilute acid without change. This 'passive' condition of iron, as it is termed, is believed to be due to the formation of a film of oxide, insoluble in acids, which protects the iron. For this reason, iron may be used instead of platinum in Grove's battery, provided that the hydric nitrate is not allowed to fall below a certain point of concentration, when an uncontrollable action is set up.

1094. There are three well-known combinations of oxygen and iron—ferrous oxide (FeO); ferroso-ferric oxide, or magnetic oxide (Fe_3O_4); and ferric oxide (Fe_2O_3). We have evidence of the existence of a fourth, which would be represented by the formula FeO_3 (analogous to chromic anhydride, CrO_3), since salts corresponding to it are known. Ferrous oxide and ferric oxide are representatives of distinct series of salts, which will be next described.

FERROUS SALTS.

(Iron diatomic, $\text{Fe}'' = \text{H}_2$).

1095. *Ferrous Oxide* (FeO).—This is not easily obtained pure, owing to its great affinity for oxygen, by union with which it passes into ferric oxide. Ferrous hydrate (FeH_2O_2) is obtained by adding caustic potash to a solution of a pure ferrous salt. Special precautions are necessary to have both solutions perfectly free from traces of air, which would at once cause the formation of a ferric salt. It is a white substance, which may be dried in an atmosphere of hydrogen; but it is scarcely possible to preserve it from oxidation.

1096. *Ferrous Sulphide* (FeS).—This is usually prepared by heating together iron filings or turnings and sulphur. Combination takes place at a low red heat, the mixture becoming incandescent, and a bronze-coloured friable mass is obtained. It is used, as already mentioned, for the preparation of hydric

sulphide, which is evolved when it is acted upon by hydric sulphate (par. 766, page 306).

1097. *Ferrous Carbonate* (FeCO_3) has been already referred to as a constituent of clay iron-stone. It also occurs in rhombohedral crystals as spathic iron ore. It is, like calcic and other carbonates, soluble in water containing carbonic dioxide, and exists in this state in many of the chalybeate springs, which are distinguished by their inky taste, and the reddish-brown deposit of ferric oxide which they form when exposed to the air.

1098. *Ferrous Sulphate* (FeSO_4).—This is the well-known salt, green vitriol, and is prepared on the large scale in the manufacture of alum (par. 1054, page 423), by the oxidation of the ferric sulphide which the alum-shale contains. The residue from the preparation of hydric sulphide (page 306) also yields, on evaporation, a very pure salt. It forms light-green crystals, which, unless carefully protected, slowly oxidise in the air. It is used in photography as a reducing agent, in the preparation of some black dyes, but, above all, in the manufacture of writing-ink and Prussian blue. Ordinary ink is made by mixing infusion of nut-galls with solution of ferrous sulphate, the black precipitate (of ferrous gallate and tannate) which forms, being kept in suspension by the addition of gum-water. In order to obtain a pure solution of ferrous sulphate, clean iron wire may be dissolved in dilute hydric sulphate in a flask fitted with a delivery-tube, as in fig. 32, page 166, the end of which dips under water. Access of air is thus prevented, and the salt is kept in an atmosphere of hydrogen until it is wanted. The solution may be used for the experiments in the next paragraph.

1099. *Tests for Ferrous Salts*.—In order to obtain the reactions satisfactorily, a few drops of the solution of ferrous sulphate should be poured direct from the flask into a tube already containing the test solution, so as to avoid exposure to air, and the cork and tube should be immediately fitted again to the flask.

(1.) Hydric sulphide occasions no precipitate, if the solution contains free acid.

(2.) Ammonic sulphide causes a black precipitate of sulphide, which readily dissolves in very dilute hydric chloride.

(3.) Potassic hydrate gives a gray precipitate of ferrous hydrate, insoluble in excess, which, on being shaken up in the air, or poured from tube to tube, turns black, and finally reddish-brown, owing to oxidation.

(4.) Potassic ferrocyanide (yellow prussiate) gives a bluish-white precipitate, rapidly becoming dark-blue on exposure.

(5.) Potassic ferricyanide (red prussiate) gives a deep-blue precipitate of ferrous ferricyanide (see par. 1109), which is used as a paint under the name of 'Turnbull's blue.'

(6.) Potassic sulphocyanate produces no change of colour.

1100. *Ferroso-ferric Oxide* (Fe_3O_4).—This occurs native as magnetic oxide, and is formed whenever iron is heated to redness in air or oxygen. It constitutes the common black scales which are seen round a blacksmith's anvil, and is the only oxide of iron which is attracted by the magnet. It does not form any very definite series of salts, and may, in fact, be regarded as a mixture of ferrous and ferric oxides ($\text{FeO} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$): compare the red lead oxide, Pb_3O_4 , par. 1042, page 418.

FERRIC SALTS.

(Iron triatomic, $\text{Fe}''' = \text{H}_3$.)

1101. This is the most stable series of iron salts. They are formed by the oxidation (par. 1098, page 444) of ferrous salts, and are permanent in the air. Their solutions are generally yellow or brown, and have an ink-like astringent taste. They are used in medicine as tonics.

1102. *Ferric Oxide* (Fe_2O_3).—The native varieties of this substance have been already described. It is formed artificially by heating ferrous sulphate to redness, as in the manufacture of Nordhausen acid (par. 750, page 299). Ferric hydrate (FeH_3O_3) is obtained as a bulky reddish-brown precipitate when

ammonia or caustic potash is added to a solution of a ferric salt. This precipitate, when dried and ignited, shrinks greatly in bulk, and becomes insoluble, or nearly so, in acids. It is largely used, under the name of rouge, for polishing plate-glass and gold and silver ornaments. When ground up with oil, it forms the common chocolate-paint used for ironwork. It is employed in painting on glass and porcelain, the material being afterwards ignited in a kiln, so as to fix the colour, which is a fine dark-red.

1103. *Ferric Sulphide* (FeS_2).—This is the common mineral iron pyrites, often found crystallised in very perfect cubes and dodecahedra. Its employment as a source of sulphur may be illustrated by heating a little in a tube of hard glass, closed at one end, when a yellow sublimate of sulphur will be obtained.

1104. *Ferric Chloride* (FeCl_3).—This may be obtained by heating iron-wire in a current of chlorine in an apparatus similar to that shewn in fig. 76. It sublimes in brilliant greenish-black crystals, which are very deliquescent. A solution of it may be made by dissolving iron-wire in warm dilute hydric chloride, and, when the metal has disappeared, adding hydric nitrate little by little as long as any nitric oxides are evolved. The ferrous chloride at first formed passes into the condition of ferric chloride, and the solution becomes dark yellow :



This solution, containing free acid, may be used in examining the reactions of ferric salts.

1105. *Tests for Ferric Salts*.—(1.) Hydric sulphide gives a nearly white precipitate of sulphur (as in the case of chromic salts), owing to reduction of the ferric salt to a ferrous salt, the solution losing its yellow colour :



(2.) Ammonic sulphide gives a black precipitate, consisting of ferrous sulphide and sulphur.

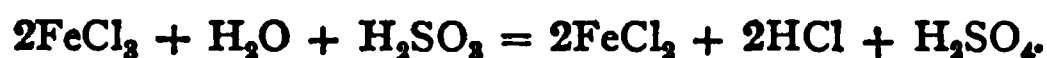
(3.) Potassic hydrate gives a reddish-brown precipitate of ferric hydrate.

(4.) Potassic ferrocyanide gives, even in extremely dilute solutions, a deep-blue precipitate of Prussian blue.

(5.) Potassic ferricyanide occasions no precipitate, but the solution turns green.

(6.) Potassic sulphocyanate produces a splendid blood-red coloration. This is a most delicate test for a ferric salt; when mere traces are present, the colour may be seen by placing the test-tube on a sheet of white paper, and looking down through the liquid.

1106. Ferric salts may be reduced to ferrous salts in several ways. Thus, if a little hydric sulphite is warmed with an acidified solution of ferric chloride, the solution becomes nearly colourless, and gives the reactions of a ferrous salt:



Another easy method is to place a bit of zinc in the solution, which should be strongly acid. The 'nascent' hydrogen withdraws a portion of the chlorine, and the reduction is so complete that scarcely any colour is given on addition of potassic sulphocyanate.

1107. All compounds of iron, when added to a borax bead, give in the oxidising flame a bead which is orange while hot, and yellow when cold; in the reducing flame the bead becomes green, and much lighter in colour when cold.

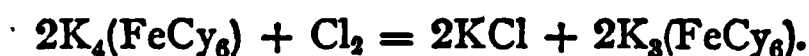
1108. *Radicles containing Iron and Cyanogen.*—When potassic cyanide is added to a solution of a ferrous salt, a precipitate of ferrous cyanide is formed which dissolves in excess of the cyanide, forming a compound in which the presence of iron cannot be recognised by the usual tests. The reaction may be thus represented:



The salt formed is the ordinary potassic ferrocyanide, the preparation of which has been given under CYANOGEN. The iron appears to be associated closely with the cyanogen, forming a compound radicle called 'ferrocyanogen.' The potassium may be replaced by other basic radicles, and thus a series of

salts called FERROCYANIDES are obtained. Of these, the only one which need be now mentioned is the deep-blue precipitate which is formed when potassic ferrocyanide is added to a ferric salt. It is a ferric ferrocyanide, represented by the formula, $\text{Fe}_4(\text{FeCy}_6)_3$, in which iron occurs in two capacities, both as a base, and also as a constituent of an acid radicle. This salt forms the common paint, Prussian blue, and is also the basis of a blue writing-ink, since it dissolves freely, when pure, in a solution of hydric oxalate (oxalic acid).

1109. When chlorine is passed into a solution of potassic ferrocyanide, the liquid becomes red, and on concentration, yields fine ruby-red prisms of a new salt :



This salt only differs from potassic ferrocyanide, so far as the results of analysis go, in containing one atom less of potassium ; but its properties and reactions are very different. It is called potassic ferricyanide ; and, just as a ferrocyanide may be regarded as formed by the action of a cyanide upon *ferrous* cyanide, so a ferricyanide may be considered as formed by the action of a cyanide upon *ferric* cyanide ($3\text{KCy} + \text{FeCy}_3 = \text{K}_3\text{FeCy}_6$). In other words, in its formation from the ferrocyanide, the iron has changed its atomicity, has become triatomic instead of diatomic. The practical importance of the salt is due to the fact, that a very fine blue precipitate, forming the paint called 'Turnbull's blue,' is produced when a solution of it is mixed with a solution of a ferrous salt.

| NICKEL. | | | COBALT. | | |
|----------------|---------|---------|-----------|---------|---------|
| | Symbol. | Weight. | | Symbol. | Weight. |
| Atom..... | Ni | 59 | Atom..... | Co | 59 |
| Density = 8.6. | | | | | |

1110. These two metals are connected together by the closest analogies. The weights of their atoms are identical. Their reactions are so similar that there is great difficulty

in separating them from each other. They always occur associated together in nature, and even in meteorolites, in which they often accompany iron. The history of their names is somewhat curious. In the German copper-mines, the men often came upon a vein which appeared like a copper ore, but which, when smelted, yielded no copper, but crumbled away to a gray ash. Such minerals they called *kupfer-nickel* and *kobold-glance*, because they thought that the nickels and kobolds, or spirits of the mine, were deluding them with bad ore. And it was not till 1750 that Cronstedt, in examining these ores, was led to the discovery of two new metals, which he allowed to retain the names given to the ores by the miners.

1111. The ores of nickel are: (1.) Kupfer-nickel, an arsenide (NiAs); and (2.) Nickel-glance, an arsenio-sulphide. Similarly, the cobalt ores are: (1.) Smaltine, an arsenide; and (2.) Cobalt-glance. The metals are obtained by rather complicated processes, the details of which will be found in books on metallurgy. It will be sufficient to say that the ores are roasted at a regulated temperature, when much of the arsenic is driven off and condensed in flues, and the residue is fused with sand and potassic carbonate. The cobalt passes into combination as a silicate, forming a blue glass, which, when ground, constitutes the 'smalt' of commerce, while the nickel compounds remain unaltered, and are found in the residue at the bottom of the pots. All the processes for the separation of the two metals depend on the fact that cobalt is oxidised more readily than nickel.

1112. The metals cobalt and nickel much resemble iron in properties. They are silver-white, hard, tough, difficultly fusible bodies, which are susceptible of magnetism, though not to the same extent as iron. Nickel is used in large quantities in the manufacture of German-silver (see par. 1004, page 402). They dissolve in acids, generally with evolution of hydrogen, forming salts in which the metals are diatomic (as iron in the ferrous salts), and which (at least in the case of nickel) shew but little tendency to become oxidised. The salts of nickel are usually

green; those of cobalt, of a blue or pink colour.* Cobalt is chiefly employed in the staining of glass, to which it imparts a beautiful blue colour, and also in painting on china and porcelain, for which purposes its oxide is employed.

1113. *Cobaltous Nitrate*, $\text{Co}(\text{NO}_3)_2$.—This is the only important salt of cobalt, and is obtained by dissolving the metal or the oxide in hydric nitrate. It is employed in the laboratory in various blow-pipe tests, in the detection, for instance, of zinc and aluminium. A solution of this salt, or, better, of cobaltous chloride, which may be easily obtained by boiling the nitrate with hydric chloride, forms a 'sympathetic ink.' The solution is rose-coloured, but, if sufficiently diluted, characters written with it on paper are invisible when dried in the air. If the paper, however, be heated before the fire, they appear of a deep blue, but again become invisible if left in the air or held in a current of steam. These changes depend on the fact that the pink, air-dried salt contains water of crystallisation, which is given off when it is heated, a blue anhydrous salt being formed, which readily absorbs moisture again, passing into the pink modification. When a salt of nickel is mixed with the cobalt salt, a green instead of a blue colour is obtained; and a wintry landscape may be painted, in which the foliage of the trees is drawn with a brush dipped in the above solution, and which, when held before the fire, puts on an appearance of summer.

1114. *Tests for Cobalt and Nickel*.—A solution of cobaltous nitrate and of nickelous sulphate, each containing 3 grms. of the salt in 20 c.c. of water, may be used.

A. Cobalt salts:

(1.) Ammonic sulphide gives a black precipitate of cobaltous sulphide, which is scarcely soluble in very dilute cold hydric chloride (1 part of the acid to 10 of water), but is dissolved by a stronger acid on boiling.

(2.) Potassic hydrate gives a light-blue precipitate, which

* It may be noticed that the colours of nickelous sulphate and cobalt nitrate are complementary to each other; so that if their solutions are mixed in proper proportions, a dusky liquid is obtained, free from positive colour.

becomes reddish-brown when the solution is boiled. It is dissolved by ammonia.

(3.) Potassic cyanide gives a light-red precipitate of cobaltous cyanide, which, like the ferrous salt, dissolves in excess of the cyanide, and, if the solution is boiled (with addition of one or two drops of dilute hydric chloride), passes into the condition of a cobalticyanide.

(4.) Compounds of cobalt impart to a borax bead a deep-blue colour, both in the oxidising and reducing flame. This is a very delicate and characteristic reaction, and serves to detect cobalt in presence of nickel.

B. Nickel salts :

(1.) Ammonic sulphide gives a black precipitate similar to that produced with the cobalt salt.

(2.) Potassic hydrate gives a light-green precipitate, unaltered by boiling, and soluble in ammonia, after being freed from the excess of potash.

(3.) Potassic cyanide gives a greenish-white precipitate of nickelous cyanide, which redissolves in excess of the cyanide as a double salt, and is reprecipitated on addition of a *slight* excess of hydric chloride, even after boiling, since no nickeli-cyanide radicle is known to exist. By this reaction, nickel can be detected in presence of cobalt, if the solutions are not very dilute. The student should verify this.

(4.) Compounds of nickel, when added to a borax bead, imparts a brownish-red colour in the oxidising flame, while the bead becomes gray and turbid in the reducing flame.

MANGANESE.

| | Symbol. | Weight. | Density = 8.0. |
|-----------|---------|---------|----------------|
| Atom..... | Mn | 55 | |

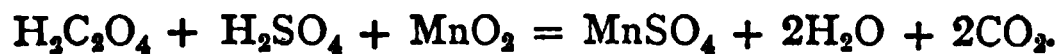
1115. This metal occurs in tolerable abundance, chiefly as an oxide in the mineral pyrolusite, or black oxide of manganese (MnO_2). The metal itself is obtained with difficulty, by intensely heating a mixture of the oxide with charcoal. It

much resembles cast-iron in appearance and physical properties, and has not yet been put to any practical use, although some of its alloys, such as that with iron, seem likely to be of value. It forms the colouring matter of the amethyst, and its oxide is used in the manufacture of glass, to which, when added in sufficient quantity, it imparts a purple colour. It forms several series of compounds, in general analogous to those of chromium and iron, but differing in this respect—that the manganous salts are more stable than the manganic salts, whereas the contrary is the case with chromium and iron. We shall begin by describing the substance from which all the other manganese compounds are prepared.

1116. *Manganic Dioxide* (MnO_2).—This is the well-known black oxide of manganese, which has been already referred to under OXYGEN and CHLORINE. It is found abundantly, as 'pyrolusite,' in various parts of Germany, and in Devonshire. It owes its great value to the readiness with which it parts with some or all of the oxygen it contains. Formerly, it was the usual source of oxygen gas, since, when heated to redness, it is decomposed into oxygen and a lower oxide, corresponding to the magnetic oxide.



And, although this process is now seldom employed, the substance is still used to mix with potassic chlorate, as it has the property of causing the decomposition of the latter salt at a comparatively low temperature. It is used in enormous quantities for the production of chlorine in the manufacture of bleaching powder and potassic chlorate. The following experiment will illustrate another oxidising action of the substance. If some powdered hydric oxalate is mixed with dilute hydric sulphate, no action occurs; but, on addition of a little manganic dioxide, an effervescence begins, and carbonic dioxide is evolved, owing to the decomposition of the oxalate:



This is the basis of the process employed in determining the

value of a sample of commercial manganese. A known weight of it is caused to act upon excess of hydric oxalate and hydric sulphate in a weighed flask, and the amount of carbonic dioxide given off is ascertained by weighing the flask after the action is over. The purer the manganese, the more carbonic dioxide will be evolved by the action of a given weight of it.

1117. Manganic dioxide is acted upon without difficulty by many acids. The action, in the case of hydric chloride, may be shewn in an apparatus like that shewn in fig. 76, page 404; the bulb, *c*, being half-filled with the oxide, heated to redness, and dry hydric chloride passed over it, when water and chlorine will be produced:



In this, and most other cases, a manganous salt is formed, corresponding in composition to the ferrous salts, in which the manganese is diatomic.

1118. *Manganous Chloride* (MnCl_2).—This is the salt obtained as a residue in the manufacture of chlorine, and is useful as a source of other manganous salts. It is usually, however, contaminated by iron, from which it may be purified in various ways. The simplest, perhaps, is to evaporate the impure liquid completely to dryness, and then to heat it to low redness in a porcelain basin or crucible. By this process, the iron is either expelled as the volatile chloride, or changed into the insoluble oxide, so that when the heated mass is digested in water, only the manganese chloride dissolves. Its purity from iron may be ascertained by adding to the liquid potassic ferrocyanide, which should produce a pinkish-white, and not a blue precipitate. If the latter appears, iron is still present.

1119. *Reactions of Manganous Salts*.—A solution of the pure manganous chloride (2 grms. in 20 c.c. of water) may be taken for the following tests:

- (1.) Hydric sulphide gives no precipitate.
- (2.) Ammonic sulphide produces a flesh-coloured precipitate of manganous sulphide (MnS), soluble in dilute hydric chloride.

It changes to a dark-brown when exposed to the air, but as originally produced is quite peculiar in tint, and distinctive of compounds of manganese.

(3.) Potassic hydrate produces a precipitate of manganous hydrate (MnH_2O_2), which is at first white, but rapidly becomes buff-coloured, and finally dark brown, owing to its conversion into manganic hydrate (MnH_3O_3). These three tests are quite distinctive of manganous salts.

1120. The manganic salts corresponding to the sesquioxide (Mn_2O_3), in which the metal is triatomic, are unimportant. A manganic chloride is known, which is very unstable, passing into manganous chloride, with evolution of chlorine. Manganic oxide (Mn_2O_3) occurs native as the mineral Braunite.

1121. *Manganoso-manganic Oxide* (Mn_3O_4).—This is a very stable substance, and is produced by igniting manganic dioxide, as in making oxygen, par. 1116; or, on the other hand, by heating manganous carbonate in the air. It corresponds in composition to the magnetic oxide of iron.

1122. *Higher Oxidised Compounds of Manganese*.—Two classes of these are known; one derived from the trioxide (MnO_3), and consisting of the manganates—for example, potassic manganate (K_2MnO_4)—analogous in composition to, and isomorphous with the chromates and sulphates; the other forming the series of permanganates, which correspond to a still higher oxide, the heptoxide (Mn_2O_7), and are analogous to the perchlorates—potassic permanganate, for instance (KMnO_4), with potassic perchlorate (KClO_4).

1123. *Potassic Manganate* (K_2MnO_4).—When 4 parts of finely powdered manganic dioxide are mixed with 3 parts of potassic chlorate or nitrate, and 6 parts of potassic hydrate (the student may take the above quantities in grammes), and the whole heated to low redness in a porcelain dish or crucible, a dark-green mass is formed, consisting chiefly of potassic manganate:



This substance goes by the name of *mineral chameleon*, in

consequence of the curious changes in colour which it undergoes when dissolved in water. The student should prepare it for the sake of observing these. Mineral chameleon is of a green colour, and if dissolved in a small quantity of cold water, forms a beautiful dark-green solution. If this be slowly diluted with a large quantity of water, the green begins to exhibit shades of red; and various tints, produced by the intermixture of red, green, and blue, successively appear, till ultimately the liquid acquires a deep purple colour. These changes occur much more rapidly if the potassic manganate, dissolved in a little cold water, be afterwards diluted with the same liquid at the boiling temperature, and they are determined at once by the addition of a few drops of almost any acid. They are due to the decomposition of the manganate into a lower and a higher manganese salt. Thus, when water is employed, potassic permanganate and manganic dihydrate are formed:



When an acid is taken, potassic and manganous salts are produced, together with hydric permanganate.

1124. *Potassic Permanganate* (KMnO_4).—This salt is of great interest and importance, both in commerce and to the analytical chemist, from the facility with which it gives up oxygen. A solution of it, or of the corresponding sodic salt, is largely used under the name of ‘Condy’s fluid,’ for disinfecting purposes. Putrid liquids and solids are rapidly rendered inodorous and harmless by pouring a little of this solution upon them; but, since the salt is not volatile, it is not adapted for purifying air. In the laboratory it is used as an oxidising agent in several processes of volumetric analysis. The presence of a mere trace of it imparts a pink tint to a liquid, and hence it is easy to mark the exact point when an excess has been added to a solution capable of being oxidised. The following experiments will illustrate its properties:

(1.) When some solution of hydric sulphite is added to a dilute solution of potassic permanganate, the purple colour

rapidly and completely disappears; the hydric sulphite being oxidised to hydric sulphate, and a manganous salt being formed :



A similar change takes place when a solution of ferrous sulphate is used, and this is the basis of a process for determining the amount of iron in iron ores, a solution of permanganate of known strength being added, drop by drop, from a measuring-tube called a 'burette,' to a solution of a certain weight of the ferrous compound, until the fluid assumes a pink tint; the volume of permanganate employed is then read off, and corresponds to the amount of ferrous salt present.

(2.) When a solution of hydric oxalate is added to potassic permanganate, the liquid becomes decolourised slowly in the cold, and more quickly when it is heated; while carbonic dioxide is given off with effervescence.

1125. Manganese compounds, when fused with borax before the blow-pipe, give a bead which is violet in the oxidising flame, but loses its colour entirely when held in the reducing flame. They may also be identified by fusing them, with a little sodic carbonate, in the oxidising flame, when a bluish-green mass of sodic manganate is formed. This test is very delicate and characteristic.

COMPARATIVE VIEW OF THE OXIDES OF THIS GROUP.

| | Aluminium. | Chromium. | Iron. | Manganese. |
|------------------|--------------------------------|--------------------------------|--------------------------------|-----------------------------------|
| Monoxide..... | (?) | CrO | FeO | MnO |
| Magnetic Oxide | | | Fe ₃ O ₄ | Mn ₃ O ₄ |
| Sesquioxide..... | Al ₂ O ₃ | Cr ₂ O ₃ | Fe ₂ O ₃ | Mn ₂ O ₃ |
| Dioxide..... | | | * | MnO ₂ |
| Trioxide..... | | CrO ₃ | (FeO ₃) | (MnO ₃) |
| Heptoxide..... | | (?) | | (Mn ₂ O ₇) |

* Iron pyrites (FeS₂) corresponds to this.

URANIUM.

| | Symbol. | Weight. | |
|-----------|---------|---------|-----------------|
| Atom..... | U | 120 | Density = 18.4. |

1126. Uranium is a rare metal, and will not need a long description. Its chief source is pitch-blende, which is an oxide (U_3O_4), corresponding to the magnetic iron oxide. It greatly resembles iron in its properties, and in the compounds it forms. It is used for painting on porcelain, for which purpose ground pitch-blende is employed, the colour produced being a very intense and permanent black. It also imparts a very peculiar yellowish-green tint to glass, the more refrangible of the incident rays of light undergoing the change called 'fluorescence,' for a description of which a text-book on optics must be consulted.

GOLD.

| | Symbol. | Weight. | |
|-----------|---------|---------|-----------------|
| Atom..... | Au | 197 | Density = 19.3. |

1127. Gold is a most widely diffused metal. It is found in every country, and nearly always in the metallic state, disseminated in quartz rock, sometimes beautifully crystallised, but more generally in fine filaments or nodular masses called nuggets. Yet it is one of the most expensive metals, from the fact that it never occurs in large quantities together, but only in minute scattered deposits, from which it cannot be extracted without much labour. The chief supplies of it come from California, South America, Australia, and the Ural Mountains, and a certain amount is found in Cornwall, and in Wales, near Dolgelly. From the ease of working it, and its indestructibility, it has been known and valued from the earliest times. It is hardly necessary to mention the dreams of the alchemists, who believed that they would succeed in making gold from the 'baser' metals, by addition of a substance called the philosopher's stone, which they never succeeded in producing. Yet, in their enthusiastic search for it, they discovered many valuable

chemical facts, many of the most important compounds, and many of the most useful pieces of apparatus which we possess; and their labours, though misdirected, were almost as valuable as if they had succeeded in making gold itself. The alchemical name for gold was 'sol' or 'rex,' from which the name 'aqua regia,' for the mixture of acids which dissolves gold, is derived. The Latin name is *aurum*, whence we have the symbol for its atom, Au.

1128. The gold-dust of commerce consists of small particles of the metal, which have been washed by streams from their original position in the veins of rocks, and which are diffused through the sands at the bottom of the rivers fed by such streams. By taking advantage of the difference in specific gravity between the gold and the sand, the latter is washed away, and the gold-dust left. The auriferous quartz rocks are stamped to coarse powder, and treated in a similar way, mercury being often used to separate the finer particles, with which it forms an amalgam, and is afterwards separated by distillation.

1129. Pure gold has a well-known yellow colour, and a brilliant lustre when polished. Its specific gravity is very high, 19.3, and it is an excellent conductor of heat and electricity. It is very soft, and exceedingly malleable and ductile. It is obtained in the thin sheets called 'gold-leaf,' by being placed between layers of an animal membrane ('gold-beater's skin'), and beaten for several hours with heavy broad-faced hammers upon blocks of polished marble. These leaves are only $\frac{1}{10,000}$ th of a millimetre in thickness, and are so thin as to be transparent. If a gold-leaf is laid flat upon a plate of glass, and held up to the light, it will be seen to transmit the green rays.* Gold may also be drawn into wire finer than a hair; but the finest wire has been obtained by Dr Wollaston's process, which consists in covering a wire of gold with a tube of silver, drawing out the two together into fine wire, and then dissolving away

* These rays are really transmitted through the substance of the metal, and not through holes in it; as is proved by the fact that the transmitted light, when passed obliquely through the film, is changed in character, becoming polarised; an effect which is produced by passage through a transparent body, but not through interstices in an opaque film.

the coating of silver by hydric nitrate, which leaves the core of gold untouched. In this way, a wire has been obtained scarcely thicker than gold-leaf. Gold melts at about the same temperature as copper, a bright red heat. It forms alloys with most metals; that with copper is employed for jewellery and coinage, pure gold being too soft to be used alone. The composition of these alloys is always expressed by stating how many parts out of 24 parts, or carats, are pure gold. Thus the alloy used for gold coins is 22 carats fine—that is, out of every 24 grms. 22 grms. are pure gold, and 2 grms. copper. Mercury readily unites with gold, forming an amalgam which is used in gilding. But articles are now usually gilt by electric action; the process is similar to that of electrotyping (page 96), a solution of auric cyanide being substituted for the copper salt.

1130. Gold is not acted upon by oxygen or sulphur at any temperature, nor is it dissolved by any of the ordinary acids. Chlorine acts upon it readily, forming auric chloride; and a mixture of hydric nitrate and hydric chloride (which, as has been mentioned, evolves chlorine, par. 674, page 267) is usually employed to dissolve the metal. This may be illustrated by placing four or five leaves of gold in each of two beakers, and adding to the one a little hydric nitrate, and to the other a little hydric chloride. Neither of them will dissolve the metal, even on applying heat; but if the contents of the beakers are mixed, the gold quickly disappears, and a yellow solution is formed.

1131. *Auric Chloride* (AuCl_3).—This is the substance formed in the experiment just mentioned, and is the only important salt of gold. If the solution is evaporated, at a temperature not much above boiling water, it will yield a crystalline mass of the chloride, which is very deliquescent, soluble in water, alcohol, and ether, and readily decomposed by heat or light. It stains the skin, or other organic tissues, purple, if they are wetted with its solution, and left for some time in daylight. Metallic gold is separated from it by almost any reducing agent. An interesting example of this reduction is afforded by Faraday's 'ruby gold.' When a few drops of a solution of

phosphorus in ether are added to an extremely dilute solution of auric chloride, the liquid gradually becomes of a splendid red colour, from the precipitation of very fine particles of metallic gold. These particles will remain suspended in the liquid for months, the red colour being unaltered; but the addition of a little sodic chloride is sufficient to cause the aggregation of the gold, which soon falls to the bottom as a purple powder, and the solution becomes colourless. Gold, in a similar finely divided condition, is the colouring matter of the well-known Bohemian ruby glass. Auric chloride forms a double salt with sodic chloride, which is used for toning photographic prints (par. 934, page 376).

1132. *Aurous Chloride* (AuCl).—This substance, which is an example of a series of salts in which gold is monatomic, is formed by carefully heating auric chloride to a temperature of 250° , when a portion of its chlorine is expelled.

1133. *Tests for Gold*.—The solution of auric chloride obtained in the experiment given in par. 1130 may be used, any great excess of acid being driven off by evaporation.

(1.) Hydric sulphide gives a black precipitate of auric sulphide (Au_2S_3), which dissolves on addition of ammonia and ammoniac sulphide.

(2.) Ferrous sulphate produces a precipitate of metallic gold, which appears brown when looked at by reflected light, but bluish-green when the tube containing it is looked through so as to see it by transmitted light. If it is collected on a filter, dried, and rubbed with any smooth body, it will exhibit the characteristic yellow colour and lustre of the metal. This is a good method of separating gold from other metals, which are (as a rule) not precipitated by ferrous sulphate.

(3.) The addition of a few drops of stannous chloride causes a purple-red precipitate, containing tin and gold, which has long been known under the name of the purple of Cassius, and is employed in painting on porcelain.

THALLIUM.

| | | | |
|------------|---------|---------|-----------------|
| Atom | Symbol. | Weight. | Density = 11.9. |
|Tl | | 204 | |

1134. The discovery of this metal in 1861, which was one of the first-fruits of the employment of the spectroscope, has been already alluded to (page 82). Since then, it has been obtained in considerable quantity, and its compounds have been studied by M. Lamy, among others, who discovered the metal independently, very shortly after Mr Crookes. It derives its name from the Greek *θαλλός*, a green bough, from the bright-green light emitted by its compounds when introduced into the flame of a Bunsen burner. This light in the spectroscope is seen to consist of a single well-defined green ray (fig. 21, page 79), constituting the simplest spectrum given by any element, and is a most characteristic and delicate test for the presence of thallium. The usual source of the metal is iron pyrites, which, when roasted to supply sulphurous anhydride in the manufacture of hydric sulphate, gives off also vapours of thallic oxide, which condense in the flues, and may be dissolved out of the residue by boiling with water containing hydric nitrate. From this solution the thallium is precipitated as chloride, the latter salt is converted into sulphate, and the metal is obtained by placing in the solution of thallic sulphate a rod of zinc, upon which metallic thallium is deposited in brilliant plates, like lead under similar conditions.

1135. Thallium is a very soft, brilliant, white metal, much resembling lead in physical properties, such as density, want of elasticity, melting-point, &c. It is very rapidly tarnished in air, forming thalious oxide (Tl_2O), which is soluble in water, forming a solution of thalious hydrate which is very similar in properties to potassic hydrate. In chemical properties, thallium is curiously intermediate between the alkali-metals, such as potassium, on the one hand, and lead or gold on the other. It forms at least two series of salts :

(1.) *Thallous Salts*, such as the oxide (Tl_2O), the chloride (TlCl), and the sulphate (Tl_2SO_4), the last-named giving with aluminic sulphate a double salt, analogous to ordinary alum. In these salts, thallium is monatomic, and they closely resemble the corresponding potassic compounds, except in the case of the chloride, which is only slightly soluble in water, like lead chloride.

(2.) *Thallic Salts*—for example, thallic oxide (Tl_2O_3) and chloride (TlCl_3), the metal in these being triatomic, like gold. All thallium compounds are very poisonous; they may be most easily recognised by the spectrum reaction.

MOLYBDENUM AND TUNGSTEN.

1136. These two rare metals need only a short description. Molybdenum occurs in Norway as a sulphide, a mineral resembling graphite in appearance. From this, when roasted in the air, is obtained molybdic trioxide, or anhydride (MoO_3), which forms salts called molybdates, analogous to the chromates and sulphates. Of these, ammonic molybdate $(\text{H}_4\text{N})_2\text{MoO}_4$, is an example, and is used in the laboratory as a test for phosphates, with which its solution in hydric nitrate gives a yellow precipitate.

1137. Tungsten is found in the mineral wolfram, whence its symbol, W, is derived, and which is a ferroso-manganous tungstate, $\text{FeMn}(\text{WO}_4)_2$. Its chief oxide is the trioxide, or tungstic anhydride (WO_3), which forms a series of tungstates. When wolfram is fused with sodic carbonate, sodic tungstate (Na_2WO_4) is obtained, which is used as a mordant in dyeing, and has the property of rendering linen fabrics unflammable, when they are soaked in a solution of it.

Section V.—Tetratomic Metals.

TIN.

| | | | |
|-----------|---------|---------|----------------|
| | Symbol. | Weight. | Density = 7.3. |
| Atom..... | Sn | 118 | |

1138. Tin was one of the metals earliest discovered, and probably from the date of its discovery down to the present time, Cornwall has been the chief source of it, since the Phœnicians are said by Herodotus to have imported it from the Cassiterides, now the Scilly Islands, in which the adjacent mainland was no doubt included. From its Latin name, *stannum* (given to it from the ease with which it melts), is derived the symbol for its atom, Sn, and names for its compounds.

1139. The only important ore of tin is the dioxide, or tin-stone, which occurs in Cornwall and Malacca, both in veins and in river deposits (stream-tin). It first undergoes a laborious process of sorting, stamping, and washing, to separate earthy impurities, and is then mixed with charcoal, and reduced in a reverberatory furnace. The crude metal is refined by a process called liquation, which consists in gradually heating the ingots on a hearth, when the pure metal melts first, and is run into moulds, while the less fusible impurities, such as iron and copper, remain as a skeleton. This refined tin is further purified by a process similar to the poling of copper, and finally the blocks are heated just below their melting-point, and dropped from a height upon an iron plate, when they split up into crystalline fragments, called 'grain tin.'

1140. Pure tin is, next to silver, the whitest of the metals. It is very malleable, and may be rolled out into the thin sheets known as 'tin-foil.' A bar of it, when bent, produces a peculiar crackling or creaking sound, owing to its crystallised condition, the sound being caused by the friction of the crystals against one another, while the bar becomes sensibly warm. Tin melts at 235°, and enters into the composition of several

useful alloys, which have been already described; such as bronze (page 402), pewter, plumbers' solder (page 418), silvering amalgam (page 408). It is extensively used for coating copper and iron vessels to protect them from corrosion, and in making tin-plate (page 442). The crystalline character of tin may be well shewn by washing the surface of a piece of tin-plate, first with alcohol, to remove grease, and then with a mixture of equal parts of hydric nitrate and chloride, diluted with 8 or 10 times its volume of water, and warmed. This mixture acts unequally upon different portions of the crystalline film, and the surface soon assumes a marbled appearance, like watered silk, owing to the reflection of light from the faces of the crystals. This *moirée métallique*, as it is called, was formerly much used for ornamenting articles made of tin-plate.

1141. Tin is only very slightly tarnished by exposure to air, and is but little acted on by dilute acids. When heated much above its melting-point, it burns in the air, forming a white substance, stannic oxide (SnO_2). It is acted upon with difficulty by strong hydric sulphate; the most concentrated hydric nitrate does not act upon it at all (compare what is said of the passivity of iron, par. 1093, page 443), but if the acid is slightly diluted, a violent action takes place, and insoluble stannic hydrate is formed. Strong hydric chloride dissolves the metal pretty readily, especially when warmed, with evolution of hydrogen. Two series of salts of tin are known—namely (1), Stannous salts, in which the element is diatomic; and (2) Stannic salts, in which it is tetratomic. The chlorides and the oxides are the only salts which will need description.

1142. *Stannous Chloride* (SnCl_2) is obtained by dissolving tin in hot hydric chloride, the metal being kept in excess. The solution, when concentrated, yields crystals which form the 'tin salts' used by dyers as a mordant. When solution of potassic hydrate is added to it, a white precipitate of stannous hydrate (SnH_2O_2) is formed, which has, like aluminic hydrate, a great attraction for colouring matters. From this hydrate, stannous oxide (SnO) may be obtained by heating it out of contact of

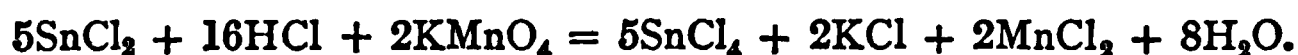
air. Stannous chloride is a powerful reducing agent, as it has a great tendency to absorb more chlorine, and pass into the condition of a stannic salt. This property will be illustrated in speaking of its reactions.

1143. *Reactions of Stannous Salts.*

(1.) Hydric sulphide produces a dark-brown precipitate of stannous sulphide, insoluble in hydric chloride, but readily soluble on addition of ammonia and ammoniac sulphide. If an acid is added to this solution, a yellow stannic sulphide is precipitated.

(2.) Mercuric chloride gives a white precipitate of mercurous chloride, rapidly turning gray, owing to reduction to mercury (see under MERCURY, par. 1029, page 413).

(3.) When some solution of stannous chloride, containing excess of hydric chloride, is added to a solution of potassic permanganate, the deep purple colour of the latter disappears, owing to its reduction to a manganous salt :



In this case, and in some others, the hydrogen of the hydric chloride is the real reducing agent.

(4.) Auric chloride produces a precipitate of the purple of Cassius (see under GOLD, par. 1133, page 460).

1144. *Stannic Chloride* (SnCl_4).—This may be obtained in solution by passing chlorine through a solution of stannous chloride, or by dissolving tin in cold aqua regia. It is largely used in dyeing, like stannous chloride. It is procured in the anhydrous condition by heating a mixture of tin filings and mercuric chloride, when a colourless liquid distils over, which emits dense fumes in the air owing to its affinity for water. It boils at 120° , and its vapour density is 9.1, which confirms the formula given above.

1145. *Stannic Oxide* (SnO_2) may be prepared, as already noticed, by the direct union of tin with oxygen, or by heating either of the stannic hydrates to redness. It is a white, hard, crystalline powder, which is extensively used for polishing

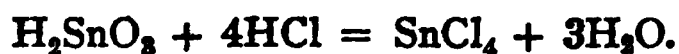
marble and glass, under the name of 'putty powder.' It is insoluble, or nearly so, in acids; but when fused with potassic hydrate, forms a soluble salt, potassic stannate (K_2SnO_3), which is used by dyers as a mordant. When a solution of potassic hydrate is added to a stannic salt, a gelatinous precipitate of stannic hydrate is produced:



This hydrate seems able to act both as an acid and as a base, and is analogous in several respects to silicic hydrate. Thus, it dissolves in excess of potash, forming potassic stannate:



and also in acids, such as hydric chloride, when a stannic salt is formed:



A remarkable modification of stannic hydrate is obtained by the action of hydric nitrate upon tin. When moderately strong hydric nitrate is poured on tinfoil, it acts violently on the metal, converting it into a white powder, the formula of which is said to be $\text{H}_{20}\text{Sn}_5\text{O}_{20}$, and which is called metastannic hydrate. It is scarcely soluble in acids, but forms with alkalies a series of salts called metastannates. Thus, tin, like silicon, seems to form a variety of hydrates, probably in consequence of the high atomicity of the elements.

1146. *Reactions of Stannic Salts.*

(1.) Hydric sulphide forms a yellow precipitate of stannic sulphide, insoluble in hydric chloride, soluble on addition of ammonia and ammoniac sulphide.

(2.) No precipitate is formed on addition of mercuric chloride. This serves to distinguish a stannic from a stannous salt.

1147. All compounds of tin, when heated with sodic carbonate on charcoal before the blow-pipe, yield a malleable metallic globule, with a white incrustation of oxide.

TITANIUM.

1148. Titanium is a rare metal, chiefly interesting from its analogy to tin in the compounds it forms. It occurs as oxide (TiO_2) in the mineral rutile, and also in many iron ores. Neither it nor its compounds have been as yet put to any practical use.

PLATINUM.

| | Symbol. | Weight. | |
|------------|---------|---------|-----------------|
| Atom | Pt | 197 | Density = 21.5. |

1149. Platinum, or, as it was originally named by the Spanish Americans, platina, in allusion to its silvery lustre—from the Spanish *plata*, silver—is comparatively a rare metal, found in South America, Russia, and Ceylon, associated with palladium, rhodium, iridium, osmium, and a little iron. It is extracted from this alloy by dissolving the latter in aqua regia, evaporating the solution to dryness, and heating the residue more strongly, when the osmium volatilises as oxide, and the iridium is converted into an insoluble chloride. The residue is then dissolved in water, and ammoniac chloride added to the solution, which precipitates the platinum as an insoluble double salt, ammoniac platonic chloride (see par. 1153). When this salt is ignited, a porous mass of finely divided platinum is left. Formerly there was great difficulty in obtaining a compact piece of metal from this ‘spongy platinum,’ as it is called, owing to its infusibility. The highest heat of a forge could not fairly melt it, but could bring it into a pasty condition, in which it was welded by hammering, like iron. But great improvements have been introduced by M. Deville, who employs the heat of a large oxyhydrogen blow-pipe, and has thus obtained large masses of platinum melted in crucibles of lime, and cast in moulds of graphite.* Much of the platinum

* In the Exhibition of 1862, an ingot of platinum was shewn weighing more than 100 kilogrammes, retaining casts of all the crevices of the mould, and thus shewing that the metal had been rendered perfectly liquid.

of commerce is obtained by simply melting the native alloy, which contains about 80 per cent. of platinum. The mixture of platinum, palladium, and iridium thus procured is harder than pure platinum, and is equally useful for many purposes.

1150. Platinum is a bright, silver-white metal, very malleable, and at least as ductile as gold. The finest wires of it have been procured by the process mentioned under GOLD (par. 1129, page 458). It resembles iron in tenacity and in its inferior conducting power for heat and electricity. It expands by heat less than any other metal, its expansibility being nearly equal to that of glass, so that platinum wires can be permanently fused into glass tubes, a fact which is often taken advantage of in the construction of apparatus. It melts at a temperature estimated at 2000° , and does not combine with oxygen at any temperature; nor is it acted on by the ordinary acids or by the immense majority of chemical reagents. It is a metal, accordingly, of the greatest value to the chemist, from its two-

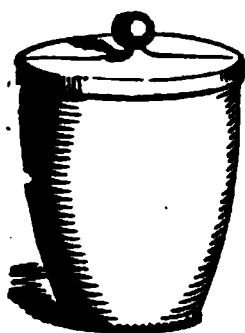


Fig. 78.

fold power of resisting high temperatures and chemical action. Crucibles made of it are constantly in use in the performance of analysis (see fig. 78); and although it is some five times more costly than silver, large vessels of platinum are employed in the concentration of hydric sulphate.* For blow-pipe experiments, platinum wire and foil are continually employed, and sheets of it are used as the negative metal in Grove's battery (page 90). The peculiar properties of finely divided platinum will be given in par. 1154.

1151. Platinum forms two series of salts, platinous salts, such as the chloride (PtCl_2), in which it is diatomic, and platonic salts, such as platonic chloride (PtCl_4), in which it is tetratomic. It will be observed that these are analogous to the two series of

* The student should remember, however, not to heat in a platinum vessel any of the following bodies: Substances likely to evolve chlorine or sulphur; caustic alkalis or alkaline earths; cyanides, chlorates, nitrates; easily reducible metallic salts, such as those of lead, silver, or tin.

tin salts in formulæ, while in properties they rather resemble those of gold.

1152. *Platinic Chloride* (PtCl_4) is the only important salt of platinum, and is prepared by dissolving the metal in aqua regia, and evaporating the liquid to dryness at a temperature not much exceeding 100° . It is a brownish-red substance, very deliquescent, and soluble in water. When it is heated to about 200° , it gives off half the chlorine it contains, and leaves a residue of *platinous chloride*, an olive-green substance insoluble in water.

1153. Platinic chloride is, it will be remembered, used as a test for potassium and ammonium, owing to its property of forming insoluble salts with the chlorides of those metals. Thus, when a solution of ammonic chloride is added to a solution of platinic chloride, a yellow crystalline precipitate of ammonic platinic chloride (sometimes called ammonic chloroplatinate) is produced :



This may be washed on a filter with dilute alcohol, in which it is even less soluble than in water. Its chief interest lies in the fact that when it is heated to low redness, ammonic chloride and chlorine are given off, and a gray, loosely coherent mass of finely divided platinum is left. This is 'spongy platinum,' which has been often referred to as an agent for producing various chemical actions; for example, the union of hydrogen with oxygen (page 185), of sulphurous anhydride with oxygen (page 298), and the decomposition of hydric peroxide (page 388).

1154. Platinum can be obtained in a still finer state of division, when it is called 'platinum black.' This is procured by adding sugar and an excess of sodic carbonate to solution of platinic chloride, and then slowly raising the liquid to the boiling-point, with occasional shaking. The metal separates as a black powder, which should be thoroughly washed and dried on a filter. Platinum in this condition is even more

active than spongy platinum in determining chemical change. This property, which is shared to a certain extent by platinum in the massive form (see par. 546, page 213), is believed to be due to the power possessed by the metal of condensing gases upon its surface, and thus bringing their particles into very close proximity. It is found that platinum black will absorb about 250 times its bulk of hydrogen, and the gas must be retained by a force equivalent to enormous pressure, and may possibly be in the liquid state.*

1155. One additional experiment illustrative of this property of platinum may be given. A few drops of strong alcohol are placed in a wide-mouthed bottle, and shaken up to diffuse the vapour; a ball of spongy platinum,† or a close spiral of platinum wire, is heated to low redness, and introduced into the mixture of alcohol vapour and air. The metal continues to glow for some time, and pungent vapours of aldehyd, together with an acid (hydric acetate), are formed, owing to the oxidation of the alcohol. A flameless lamp, and also a perfume-distributor constructed on this principle, may be met with in the shops.

1156. *Tests for Platinum.*—Platinic salts give a black precipitate with hydric sulphide, insoluble in hydric chloride, soluble in ammoniac sulphide. But the most characteristic test is the formation of the yellow crystalline ammoniac platinic chloride, on addition of ammoniac chloride.

PALLADIUM, IRIDIUM, OSMIUM, RHODIUM, RUTHENIUM.

1157. These metals are found in small quantities associated with platinum, as already mentioned, but none of them are of much practical importance. An alloy of iridium with platinum, which is extremely hard, has been used for pen-points. Palladium has acquired interest since the experiments of

* Charcoal (par. 576, page 223) has a similar property, and also alumina, clay, and many other porous substances.

† This may be easily made by placing a small bundle of fibres of asbestos in a ring formed at the end of a piece of platinum wire, dipping it into the moist ammoniac platinic chloride, and heating it to low redness over a lamp.

Professor Graham have shewn its remarkable power of absorbing hydrogen. When a strip of palladium is made the negative electrode in an apparatus for decomposing water, it absorbs 800 or 900 times its volume of hydrogen, expanding perceptibly during the absorption. This 'occluded' gas is again given off, when the substance, which Professor Graham believed to be an actual alloy of palladium and hydrogen, is heated to redness.

*Section VI.—Pentatomic Metals: Bismuth, Arsenic, Antimony.**

1158. These three closely related elements form a group which serves to connect the metallic with the non-metallic elements. They certainly possess all the typical metallic characters—such as lustre, weight, &c.; but in most of their compounds and reactions they correspond very closely to nitrogen and phosphorus. Bismuth most resembles the metals, arsenic has most analogies to phosphorus, while antimony is intermediate between the two. The study of this group, combined with frequent reference to the elements already examined, will shew in the clearest light the 'continuity' which seems universal in nature. We scarcely ever find, whether in geology, natural history, or chemistry, two groups or species, the interval between which is not bridged over by some group or individual shewing affinities to both of them.

BISMUTH.

| | Symbol. | Weight. | |
|-----------|---------|---------|----------------|
| Atom..... | Bi | 210 | Density = 9.8. |

1159. The element bismuth is not a very abundant metal, and it has of late become very scarce. It generally occurs

* There is no very conclusive evidence that the metals of this group should be considered pentatomic. In some of their compounds—for instance, the oxides, Bi_2O_3 , As_2O_3 , Sb_2O_3 —their atoms do undoubtedly replace 5 atoms of hydrogen; but, in the most strongly marked and stable series of their salts, the metals are triatomic, and they shew the closest analogies to the triatomic elements nitrogen and phosphorus. Either, then, these latter should be considered pentatomic, or the former should be placed in the triatomic group.

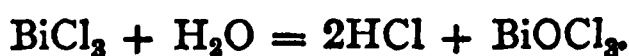
in the native state, and the chief supply comes from Saxony, where veins of it are found in gneiss and clay-slate. To obtain the metal, it is only necessary to heat the ore in iron tubes placed in a sloping position in a furnace, when the bismuth fuses, and runs into pots placed under the lower ends of the tubes. It is a crystalline, brittle metal, having a white lustre, with a distinct shade of red. It may be obtained in very perfect cubes by melting some of it in a crucible, allowing it partially to solidify, and then pouring off the still liquid portion: the interior of the crucible is then found lined with crystals. It melts at 260° , and expands considerably (like water) at its solidifying point. This property it communicates to the alloys into which it enters, and hence very sharp castings are obtained by means of them. The most remarkable of these alloys is 'fusible metal,' which is procured by melting together 2 parts of bismuth, 1 of lead, and 1 of tin. A bar of this alloy, when held in a beaker of boiling water, will melt readily; and its fusibility is still further increased by the addition of cadmium, as mentioned under that metal. Bismuth is a remarkably diamagnetic metal—that is, instead of being attracted by a magnet, like iron, it is repelled when brought near one.

1160. Bismuth forms two series of salts, in one of which it acts as a base, and is triatomic, in the other series it is pentatomic, and appears to possess feebly marked acid (or electro-negative) properties.

1161. *Bismuthous Oxide* (Bi_2O_3).—This is formed when the metal is heated in the air, but is more generally prepared by igniting the nitrate. It is a pale-yellow substance.

1162. *Bismuthous Nitrate*, $\text{Bi}(\text{NO}_3)_3$, is the only important bismuth salt, and is obtained by dissolving the metal in hydric nitrate, slightly diluted. The solution is decomposed when diluted with a large quantity of water, an insoluble basic nitrate (a nitrate associated with one or more molecules of oxide) being precipitated as a white powder. This decomposibility by water is a very characteristic property of the salts of bismuth,

and is shewn in the highest degree by bismuthous chloride. Thus, if a few drops of hydric chloride are added to a strongly acid solution of bismuthous nitrate, a portion of chloride is formed; and if a little water is now added, a white precipitate of oxychloride is at once produced:



1163. *Bismuthic Oxide* (Bi_2O_3) is obtained by passing chlorine through a solution of potassic hydrate in which bismuthous oxide is suspended. It is a brown powder, chiefly interesting from its analogy in composition to phosphoric anhydride: like the latter, it forms salts called bismuthates.

1164. *Tests for Bismuth.*—(1.) Hydric sulphide forms a black precipitate of bismuthous sulphide, insoluble in hydric chloride, and also insoluble in ammoniac sulphide.

(2.) Potassic hydrate produces a white precipitate of bismuthous hydrate (BiH_3O_3), insoluble in excess.

(3.) The addition of a little hydric chloride, and then a large excess of water, produces, as already noticed, a white precipitate of oxychloride, soluble in hydric chloride, but insoluble in a solution of hydric tartrate. This last property distinguishes it from the similar precipitate formed by an antimonious salt.

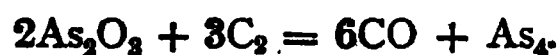
(4.) Compounds of bismuth, when reduced on charcoal before the blow-pipe, yield a brittle globule of metal, together with a light yellow incrustation on the charcoal.

ARSENIC.

| | Symbol. | Weight. | |
|---------------|-----------------|---------|---|
| Atom..... | As | 75 | 1 litre of vapour weighs 13.409 grms. Density of solid = 5.96. |
| Molecule..... | As ₄ | 300 | |

1165. Some of the compounds of arsenic, such as the sulphide, orpiment, were known to the ancients, but they do not seem to have been aware of the fearfully poisonous characters which have given the salts of arsenic a painful

interest in more modern times.* The element is sometimes found native, but is generally associated with sulphur and iron (as in mispickel, or arsenical pyrites), nickel, or cobalt, as mentioned under those metals. When these ores are roasted, as a preliminary to smelting them, the arsenic is volatilised, and condenses as arsenious anhydride (As_2O_3) in the long flues attached to the furnaces. These are occasionally swept out (a most dangerous operation), and the crude product is mixed with charcoal, and heated in crucibles provided with conical iron caps, in which the reduced metal condenses :



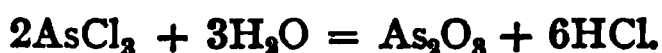
1166. Arsenic is a steel-gray, crystalline, brittle metal, the density of which is 5.9. At a low red-heat, it passes at once from the solid into the gaseous state, without becoming liquid, and forms a colourless, very heavy vapour, which condenses again in brilliant crystals, provided air be excluded, as may be done by passing a current of hydrogen through the tube in which the metal is being heated. When heated to redness in air, it burns with a bluish flame, and is converted into arsenious anhydride. The only important alloy which it forms is that with lead, which is used for making shot. A litre of the vapour of arsenic weighs 150 times as much as the same volume of hydrogen, and hence it is inferred that the molecule of arsenic is 150 times as heavy as the hydrogen molecule, or 300 times as heavy as the hydrogen atom (page 145). But chemical evidence seems to shew that the atom of arsenic is 75 times the weight of the hydrogen atom, and hence the molecule would contain four atoms, like that of phosphorus (see par. 401, page 152).

1167. Arsenic forms two series of salts, in which it is triatomic and pentatomic respectively. In its compounds it does not exhibit the strongly basic characters of a metal, but rather those of an electronegative radicle. Thus, although it dissolves in hydric nitrate, the solution does not contain

* The *aqua Tofana*, the slow poison so notorious in Italy at the end of the seventeenth century, is believed to have been a solution of arsenious anhydride in water.

arsenic nitrate, but a compound of hydrogen, arsenic, and oxygen, hydric arsenate, H_3AsO_4 , analogous to hydric phosphate (H_3PO_4). In most respects, indeed, arsenic is as closely related to phosphorus on the one hand as to antimony on the other.

1168. *Arsenious Chloride* (AsCl_3).—Arsenic unites directly with chlorine, taking fire when introduced into the gas. The chloride is usually obtained by heating a mixture of arsenious anhydride and hydric chloride, when it distils over as a colourless, dense, oily liquid, decomposed at once by water into hydric chloride and arsenious anhydride:



In the case of phosphorus, hydric phosphite is obtained; arsenious anhydride differs from the corresponding phosphorus oxide in having little affinity for water.

1169. *Arsenious Anhydride* (As_2O_3).—This is the common 'white arsenic' of the shops, and is the source of most of the arsenic compounds. It is obtained, as already mentioned, by roasting the native ores of arsenic, and is usually met with as a white flour-like powder, which volatilises, without previous fusion, at 220° . It dissolves sparingly in water, and crystallises from the solution in minute octahedra. It dissolves very readily in solution of potassic hydrate, a salt called potassic arsenite being formed:



This salt is an example of a series of salts called ARSENITES, analogous to the nitrites in formulæ, and to the phosphites in their tendency to absorb oxygen. Thus they decolourise potassic permanganate (page 455), and precipitate metallic gold from a solution of auric chloride. The properties of arsenious anhydride, and the formation of some important salts belonging to the same series, will be illustrated by the following experiments.

1170. (1.) As much of it as will lie on the tip of a penknife blade is placed at the bottom of a dry, wide test-tube (fig. 79),

and slowly heated by a small spirit-lamp held at the closed end. The arsenious anhydride changes into a colourless, inodorous vapour, and ascending in the tube, condenses in small, regular crystals, which are quite unlike those of any other white sublimate. They are distinguished by their great brilliancy and play of colours, which rival those of the diamond, and likewise by their shape, which, when perfect, is that of the regular octahedron. Entire crystals can seldom be seen, but if the sublimate be examined with a magnifying glass, equilateral triangular faces may readily be observed; and this is enough, for no crystals except regular octahedrons possess faces bounded by equilateral triangles.

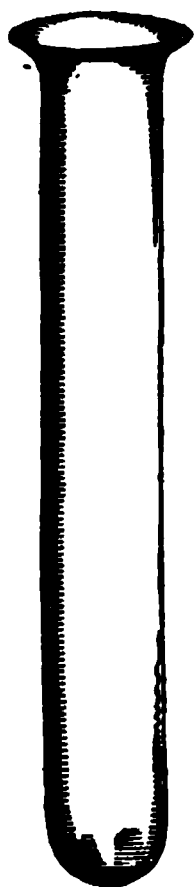


Fig. 79.

(2.) A second portion of the arsenious anhydride is mixed with dry charcoal powder and anhydrous carbonate of soda, or, still better, simply with potassic cyanide, and placed at the bottom of a tube such as is shewn in fig. 80. The mixture is introduced on a small slip of paper, so as not to soil the sides. The tube is then very gently moved backwards and forwards over a spirit-lamp, so as to expel moisture, and the drops of water which collect are wiped away by a roll of blotting-paper. The bulb is now heated to redness, when the metallic arsenic, deprived of its oxygen by the charcoal, or potassic cyanide, rises in vapour, and condenses in the narrow neck above the bulb. Here it forms a brilliant ring of a dark-gray colour as seen through the glass, but on its inner surface of a lighter tint, and rough from the projection of crystalline points.



Fig. 80.

(3.) The narrow neck containing the ring of arsenic is cut off by a file, and introduced into a wide test-tube, which is then heated over a spirit-lamp. The small tube rapidly becomes empty and transparent, as the arsenic rises out of it in vapour, and meeting with abundance

of air, combines with its oxygen to form arsenious anhydride, which condenses in its characteristic brilliant octahedral crystals in the cool part of the tube.

(4.) A third portion of arsenious anhydride is boiled for a short time with water and a little sodic carbonate, and the liquid, which is a solution of sodic arsenite, is then filtered. Three test-tubes are one-third filled with this solution.

(a.) To the first, hydric chloride and then a little hydric sulphide are added, when a bright-yellow precipitate of arsenious sulphide is formed, which dissolves in ammonia and ammoniac sulphide (see par. 1172), and is thus distinguished from cadmic sulphide. This body is also called orpiment, and is the basis of the pigment king's yellow, which is frequently used to poison flies, but is too deadly a substance to make its employment advisable for this purpose in places where children can have access to it.

(b.) To the second tube a solution of argentic nitrate, which has been mixed with *just* enough ammonia to redissolve the oxide at first precipitated, is added. It produces a primrose-yellow precipitate of argentic arsenite (AgAsO_2). (c.) To the third tube a solution of cupric sulphate is added. It produces a bright-green precipitate of cupric arsenite, which is much used as a pigment known as Scheele's green.*

1171. These tests are amply sufficient for the identification of arsenious anhydride, when it is obtained in the state of a powder, or dissolved in a colourless liquid; but in coloured solutions, such as tea, coffee, or porter, the liquid tests would be of no value. The following process is adopted for such liquids, and is also applicable to colourless solutions. To illustrate its application, solution of arsenious anhydride may be added to coffee or porter. The liquid is then transferred to a flask, and a little hydric chloride, and some small pieces of pure copper-wire, or copper-leaf, or thin sheet-copper, added to it.

* Many of the green patterns used in wall-papers are formed with this substance, and illness has been traced to particles having been rubbed off and diffused in the air. Its presence may be detected by placing a drop of ammonia on the paper, when, if copper (and therefore cupric arsenite) is present, a blue stain will be formed.

The contents of the flask are then raised to the boiling-point, and kept at this temperature for some time. The copper separates the arsenic in the metallic form, and becomes coated with a film of a steel or dark-gray colour. The pieces of blackened copper are removed from the flask, washed with a little water, and gently dried. They are then introduced into a narrow test-tube (fig. 81), and very gently heated, when the metallic arsenic volatilises from the surface of the copper, and meeting with the oxygen of the air, it combines therewith, forming arsenious anhydride. The latter deposits itself in the upper and cooler part of the tube, in the form of a ring of minute glistening crystals. A little water may then be boiled in the tube, and heat applied

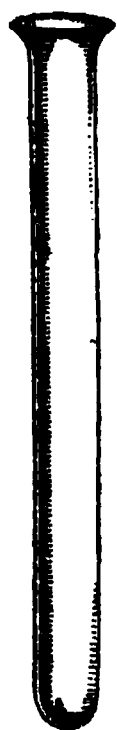


Fig. 81. till the crystals dissolve, and the solution divided into three portions, tested with the three tests (a), (b), (c), given above. This is called Reinsch's test, from the name of the chemist who proposed it.

1172. *Sulpharsenites*.—It has been mentioned that arsenious anhydride dissolves in potassic or any other alkaline hydrate, forming an arsenite. When, instead of the oxide, we take the sulphide of the metal, and instead of an alkaline hydrate we take a sulphide, such as ammoniac sulphide, a precisely analogous action takes place, and a soluble salt is obtained, called ammoniac sulpharsenite :



The sulpharsenites are simply arsenites in which oxygen is replaced by sulphur (compare KAsO_2 with KAsS_2), and other metals—namely, gold, tin, platinum, and antimony—form similar sulpho-salts ; their sulphides dissolving readily in ammoniac sulphide, as noticed in the account of their reactions.

1173. *Arsenic Anhydride* (As_2O_5).—This may be obtained by heating arsenious anhydride with hydric nitrate in excess, and further heating the residue of hydric arsenate nearly to redness. It is readily soluble in water, forming hydric arsenate (H_3AsO_4), analogous to hydric phosphate (H_3PO_4). Other

hydric arsenates ($\text{H}_4\text{As}_2\text{O}_7$ and HAsO_3) have been obtained, and series of salts are derived from them closely resembling the varieties of phosphates (page 323). The arsenates are distinguished by giving (1) a reddish-brown precipitate with argentic nitrate, to which a little ammonia has been added; (2) a granular precipitate with magnesian sulphate, previously mixed with a considerable excess of ammonia (compare the reaction of phosphates, par. 809, page 324).

1174. *Hydric Arsenide* (H_3As), or *Arsenamine*.—This remarkable body is one of the most poisonous of the compounds of arsenic, and must therefore be prepared and examined cautiously. It is procured very readily by the action of nascent hydrogen upon any of the compounds of arsenic, and its formation constitutes a most delicate test for their presence, and is the basis of the process called ‘Marsh’s test’ (from the English chemist who devised it).

1175. A small flask is fitted with a funnel and delivery tube, as shewn in fig. 82, the latter being made of hard infusible glass, and having its outer extremity turned up and drawn out to form a jet. It is advisable to introduce a short drying-tube containing calcic chloride at the point *a*, in order to dry the gas; this is not shewn in the figure. A little water and some pure zinc are placed in the flask, and hydric sulphate is added through the funnel. When the hydrogen has swept out all the air in the flask and tube (for which about two minutes should be allowed), one or two drops of the solution of sodic arsenite may be added and washed down the funnel with a little water. Hydric arsenide is at once formed, and if lighted at the jet, is seen to burn with a grayish white flame, producing a white smoke, which is arsenious anhydride. This experiment should be tried either in the open air or with the apparatus placed under a chimney or in a good draught cupboard.

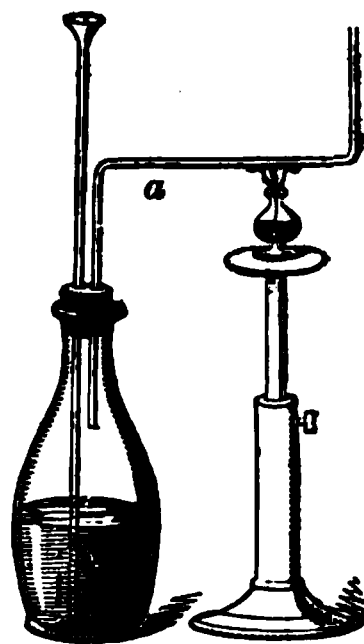


Fig. 82.

(1.) If a cold body, such as a piece of white glazed porcelain, is depressed into the flame, a black spot of metallic arsenic will be deposited, for the same reason that soot is deposited under similar circumstances from the flame of a hydrocarbon (see par. 632, page 246). Two or three spots of this arsenic soot should be formed and afterwards examined. When one of them is wetted with a drop of solution of bleaching powder, it will readily dissolve. Another may be dissolved by warming with hydric nitrate, and the solution evaporated to dryness; the residue will become of a reddish colour on addition of a trace of argentic nitrate, owing to formation of argentic arsenate.

(2.) When the tube through which the gas is passing is heated by a spirit-lamp (as shewn in the figure), a bright mirror-like ring of arsenic is formed a little in advance of the heated portion, the gas being decomposed at a low red heat into arsenic and hydrogen. If, after the experiment, a slow stream of hydric sulphide is passed through the tube, and the mirror again heated, a bright yellow sublimate of arsenious sulphide will be formed.

(3.) When the gas is passed into solution of argentic nitrate (the jet may be turned half round, and dipped into a short test-tube containing the solution), a black precipitate of silver is formed, while the arsenic enters into solution as argentic arsenite. The presence of the latter salt may be shewn by filtering the solution, and cautiously pouring upon its surface a little dilute

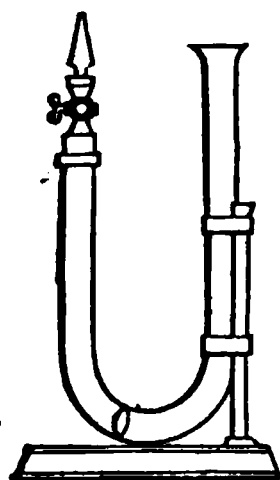


Fig. 83.

solution of ammonia from a pipette, when a yellow stratum will be formed where the solutions meet, and the liquid is neutralised.—The student should compare these reactions with those of the corresponding antimony compound (par. 1189, page 485).

1176. Fig. 83 represents an apparatus sold for the preparation of arseniuretted hydrogen. A piece of zinc is placed at the bend, and the acidulated solution of arsenious anhydride poured in. The stop-cock is kept open till the air is chased out, and then closed. The gas accumulates in the shorter limb of the

siphon, and forces the liquid past the zinc into the longer tube. In this way evolution of gas ceases, when the liquid and zinc are separated from each other. When the stop-cock is opened, the liquid returns from the long limb, and reproduces gas, forcing out what had accumulated.

1177. Both Marsh's and Reinsch's tests are often applied for the detection of arsenic in cases of poisoning. It is, of course, absolutely essential that the materials should be previously proved to be pure, since common copper, zinc, and hydric sulphate often contain arsenic. The liquid to which Marsh's test is to be applied should not contain organic matter. This may be got rid of by heating it for some time with a solution of potassic chlorate and a little hydric nitrate; or, as Dr Odling suggested, by adding an excess of hydric chloride, and distilling nearly to dryness. The distillate contains the arsenic as chloride.

ANTIMONY.

| | | |
|-------------|---------|----------------|
| Symbol | Weight. | Density = 6.7. |
| Atom.....Sb | 122 | |

1178. Antimony was discovered in the fifteenth century, but one of its compounds, the sulphide, had been known for a long period, and was, and still is, employed in the East as a pigment for darkening the eyebrows. This native sulphide, which is the mineral 'antimonite,' is very abundant in Hungary, Saxony, and other places, and is the chief ore of the metal, although the latter also occurs in combination with arsenic and silver, sometimes as a native alloy, sometimes as a double sulphide. The symbol for its atom, Sb, is derived from the Latin *stibium*, which is the old name of the pigment above alluded to, formed from antimonious sulphide.

1179. In order to obtain the metal, the sulphide is first roasted at a temperature insufficient to melt it, until the sulphur is driven off, and an impure oxide remains. This is mixed with charcoal and sodic carbonate, and fused at a low red heat in a crucible, when the metal is reduced and sinks to the bottom in

a melted state. Another method employed is to heat the powdered ore with iron filings, when ferrous sulphide and metallic antimony are formed. In either case there is a great waste of the metal owing to oxidation. Antimony occurs in commerce in large round ingots ('bowl regulus'), the surface of which is generally covered with fern-like markings, shewing very beautifully the crystalline character of the metal.

1180. Antimony has a brilliant bluish-white lustre, and is highly crystalline, and so brittle as to be readily reduced to powder in a mortar. It melts at 432° , a little above the melting-point of zinc, and may be volatilised at a bright red heat. One of its most important alloys is 'type metal,' which is composed of 4 parts of lead and 1 part of antimony. The better kinds of pewter and Britannia metal contain antimony as well as tin and lead. The presence of antimony renders the alloy hard and durable, and confers on it the property of expanding at the moment of solidification, which is of great importance in casting types.

1181. The electrical relations of antimony are peculiar: when a bar of antimony and a bar of bismuth are soldered together at one end, and the outer ends connected by a wire, if the point of junction is heated, a current of electricity is found to circulate, the outer end of the antimony being the positive pole (par. 239, page 87), and this current is maintained so long as the junction is maintained at a different temperature to the outer ends of the bars (see fig. 84). On this principle thermo-electric piles are constructed, for an account of which a text-book on Electricity must be consulted. The action seems to depend on the crystalline structure of the metals.

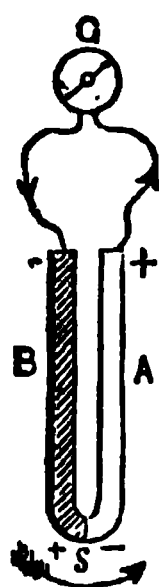


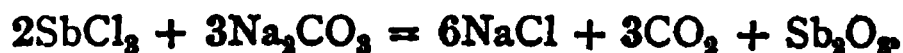
Fig. 84

1182. When antimony is heated in the air, it rapidly becomes oxidised, and at a red heat it burns brilliantly, like zinc, emitting dense white fumes of antimonious oxide. It catches fire spontaneously, as already noticed (page 261), when thrown in the state of fine powder into chlorine gas, forming the pentachloride

(SbCl_5). Strong hydric nitrate attacks it, but does not dissolve it—a white hydrate being formed, as in the case of tin. Hydric chloride scarcely acts upon it, unless it is very finely powdered; but if a little hydric nitrate is added, so as to form aqua regia, the metal rapidly dissolves, forming antimonious chloride (SbCl_3). Two series of antimony salts are known, in which the metal is triatomic and pentatomic respectively. In each series it may act either as a basic radicle, or as a component of an acid radicle, according to circumstances. Thus we have antimonious chloride (SbCl_3) and potassic antimoniate (K_3SbO_4). In this and other respects it is analogous to arsenic and phosphorus.

1183. *Antimonious Chloride* (SbCl_3).—This is prepared by dissolving the metal in hot hydric chloride, with addition of hydric nitrate in small quantities at a time. On distilling the liquid, the excess of acid passes over first, and then the chloride volatilises, and condenses in the form of a crystalline mass very deliquescent and corrosive, known as ‘butter of antimony.’ Hydric chloride dissolves it; and, when the solution is dropped into water, a white precipitate is formed of antimonious oxychloride (SbOCl_3), analogous to phosphoric oxychloride (POCl_3).

1184. *Antimonious Oxide* (Sb_2O_3) is obtained either by heating the metal in air, or by adding antimonious chloride to a hot solution of sodic carbonate:



It is a white powder, sometimes used as a paint. It dissolves readily in potassic or sodic hydrate, forming an unstable salt, one of the series of antimonites (K_3SbO_3). It also dissolves in a solution of potassic tartrate (cream of tartar, or bitartrate of potash), and the solution, on evaporation, yields crystals of a double salt, potassic antimonylic tartrate, which is the important substance tartar emetic, much used in medicine.*

* The formula of this salt is said to be $\text{K}(\text{SbO})(\text{C}_4\text{H}_4\text{O}_6)$, derived from hydric tartrate, $\text{H}_2(\text{C}_4\text{H}_4\text{O}_6)$, by the replacement of one atom of hydrogen by potassium, and another atom by a radicle, SbO , which is called antimonyl, but has not been isolated.

1185. *Antimonious Sulphide* (Sb_2S_3) has been referred to as the chief ore of antimony. The native sulphide is a dark-gray, crystalline body; but the artificial product is of a fine dark-orange colour, and is used as a paint.* The latter is procured by gently heating the sulphhydrate, which is formed as an orange precipitate when hydric sulphide is added to an antimonious salt. If the substance is heated very strongly, it turns black, and resembles the native sulphide.

1186. *Antimonic Tetroxide* (Sb_2O_4).—This oxide is only mentioned because it corresponds to an oxide in the nitrogen series, N_2O_4 . Neither of the other metals of this group form a similar oxide. It is obtained by the action of heat upon antimonic oxide, and it also occurs native as the mineral cervantite.

1187. *Antimonic Chloride* (SbCl_5) is obtained by passing dry chlorine over powdered antimony, placed in a long, sloping tube connected with a receiver. It is a volatile, nearly colourless liquid, which gives off dense white fumes in the air, owing to its decomposition by moisture into hydric chloride and hydric metantimonate:



1188. *Antimonic Oxide* (Sb_2O_5), or *Antimonic Anhydride*, may be procured by heating either of the antimonic hydrates. These latter are two in number, and correspond to two of the hydric phosphates so closely, that it seems more correct to give them names in accordance with this analogy.

(1.) *Hydric Antimonate* (HSbO_3) is obtained by the action of strong hydric nitrate upon antimony. It is a white powder, which reddens litmus-paper when moist, and dissolves in solution of potassic hydrate, forming a salt, potassic antimonate (KSbO_3), which corresponds to the nitrate (KNO_3), and the metaphosphate (KPO_3). This salt is usually procured by fusing antimony with potassic nitrate; and many other antimonates are known.

(2.) *Hydric Metantimonate* ($\text{H}_4\text{Sb}_2\text{O}_7$) is formed, as mentioned

* Compare the difference in colour of the varieties of mercuric sulphide, page 413.

in the last paragraph, by the action of water upon antimonie chloride. It corresponds to hydric pyrophosphate* ($\text{H}_4\text{P}_2\text{O}_7$), and, like the latter, is a dibasic acid, from which two series of salts are derivable. Of these, the only one which need be mentioned is potassic hydric metantimonate ($\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$), which is obtained by fusing potassic antimonate with excess of potassic hydrate. It is soluble in water, and the solution is used as a test for sodic salts, with solutions of which it gives a white granular precipitate of sodic metantimonate, the only known insoluble sodic salt.

1189. *Hydric Antimonide* (H_3Sb) or *Stibamine*.—This gas is obtained by the action of nascent hydrogen upon antimony compounds, in the same way as hydric arsenide (par. 1174), to which latter it is very analogous in properties. The student should repeat all the experiments given under the head of Marsh's test (pages 479, 480), using an antimony instead of an arsenic salt. It will be found that:

(1.) The spot on the porcelain is scarcely soluble in solution of bleaching powder. It is oxidised by hydric nitrate, but the white residue does not become red when tested with argentic nitrate.

(2.) The mirror in the tube is darker and less volatile than the arsenic mirror, and yields an orange sublimate when heated in hydric sulphide.

(3.) When the gas is led into argentic nitrate, the antimony is wholly precipitated as argentic antimonide (Ag_3Sb), and none can be detected in solution. Arsenic and antimony may be separated in this way.

1190. The analogy in composition of stibamine (H_3Sb) and arsenamine (H_3As) to ammonia (H_3N) and phosphamine (H_3P), should be noticed. The first two, however, do not shew the alkaline properties of ammonia, and are very readily decomposed by heat. Phosphamine is also decomposed by heat, and exhibits feeble alkaline and basic properties. All of them,

* It is unfortunate that the name for this substance should not have been chosen in accordance with this analogy.

except ammonia, are powerful reducing agents, as shewn by their action on salts of silver and gold.

1191. *Tests for Antimony.*—To observe these, a saturated solution of potassic antimonylic tartrate ('tartar emetic') may be taken.

(1.) On addition of hydric sulphide, an orange-red precipitate of sulphide is formed, the colour of which is highly characteristic. If a little of the liquid in which the precipitate is suspended is poured into another tube, neutralised by ammonia, and then mixed with ammoniac sulphide, the precipitate will dissolve, a sulphantimonite being formed, analogous to the sulpharsenite (par. 1172, page 478).

(2.) The precipitate formed in the last experiment should be filtered, washed, and transferred to a test-tube, by a spatula or paper-knife, while still moist. If strong hydric chloride is added, and heat applied, the precipitate will dissolve, with evolution of hydric sulphide. If a few drops of the solution of antimonious chloride thus obtained are poured into some water in another test-tube, a white precipitate of oxychloride is formed, which (unlike the analogous bismuth salt) is readily soluble in hydric tartrate.

(3.) Small quantities of antimony are detected by the formation of hydric antimonide already described. The student may add a single drop, or less, of the solution of tartar emetic to the liquid in the flask of a Marsh's apparatus, and observe that this is sufficient to give the reactions mentioned in par. 1189.

(4.) Compounds of antimony, when mixed with sodic carbonate or potassic cyanide, and reduced on charcoal, yield a brittle globule of antimony, which readily becomes oxidised in the outer flame, emitting white fumes, and covering the charcoal with a white incrustation.

1192. The relations between the group of elements, comprising nitrogen, phosphorus, arsenic, antimony, and bismuth, are so well marked and instructive, that the student will do well

to make out an extended account of them for himself. The chief points of analogy to be observed will be :

A. *Physical*.—Appearance ; condition ; relations to heat, electricity, &c. ; density of solid and of vapour.

B. *Chemical*.—Atomic weights ; composition and properties of—

(1.) *Oxides*.—Their number, basic or acid characters, stability, &c.

(2.) *Chlorides*.—Their formation and decompositions.

(3.) *Hydrides*.—Their condition, stability, basic power.

QUESTIONS AND EXERCISES.*

CHAPTER I.

1. What is the special province of the chemist in the study of matter?
2. Distinguish between analysis and synthesis, giving one example of each.
3. How many elements are at present recognised to exist? Is it likely that their number may be increased?
4. What different forces are employed by the chemist? Give examples.

CHAPTER II.

1. What is believed to be the constitution of matter?
2. What are the three states of matter? Give illustrations of the passage of a substance from one state to another.
3. State and illustrate the law of gravitation.

CHAPTER III.

1. Define 'mass' and 'weight.'
2. Describe minutely a chemical balance, giving the conditions necessary for its perfect action, and the mechanical contrivances by which they are secured.
3. What are the requisites for a good system of weights and measures? How are they fulfilled in the metric system?

* All answers to be *written* out, and given fully, not in the words of the book, if it can be avoided.

4. Give a table of the measures of volume on the metric system, shewing how they are connected with the measures of length.

5. How many centimetres are there in 3 kilometres?

Ans. 300,000.

6. How many decimetres are there in .08 of a hectometre?

Ans. 80.

7. How many litres are there in a cubic metre? *Ans.* 1000.

8. A room is eight metres long, 5 metres broad, and 3.5 metres high. How many litres of air will it contain?

Ans. 140,000.

9. A cistern is 2.8 metres square, and 1 metre deep. How many kilogrammes of water will it hold? *Ans.* 7840.

10. Define 'specific gravity.' What substances are taken as the standard of specific gravity of solids, liquids, and gases respectively?

11. The density of oxygen is 1.105. What is its density on the hydrogen scale, if the density of hydrogen = 0.0693?

Ans. 15.95.

12. Calculate the density of carbonic dioxide from the following data :

Weight of globe full of air = 1272.67 grms.

" exhausted = 1260 grms.

" filled with the gas = 1279.27 grms.

Ans. 1.52 (the temperature and pressure are assumed to be constant).

13. What is the capacity of the globe used in the above experiment, if a litre of air weighs 1.293 grm.? *Ans.* 9.8 litres.

14. Calculate the density of alcohol vapour from the following data :

Weight of flask at 18° = 50.8 grms.

" filled with vapour = 50.8245 grms.

Temperature of flask at the moment of sealing = 167°.

Capacity of flask = 351.5 c.c.

Ans. 1.599.

15. Calculate the density of liquid alcohol from the following data :

Weight of flask empty = 14.326 grms.

" filled with water = 29.654 grms.

" filled with alcohol at the same temperature = 26.741 grms.

Ans. 0.809.

16. Describe the construction and use of the hydrometer.

17. Calculate the density of copper from the following data :

Weight of copper in air = 11.809 grms.

" water = 10.490 grms.

Ans. 8.95.

18. Calculate the density of a piece of wood from the following data :

Weight of wood in air = 25.35 grms.

" a copper sinker = 11.00 grms.

" wood and sinker in water = 5.1 grms.

Density of copper = 8.95.

Ans. 0.844.

CHAPTER IV.

1. What is a crystal? By what different processes may substances be obtained in a crystalline form?

2. Enumerate the different crystallographic systems, giving one example of each, and shewing by a diagram the position of the axes.

3. Define isomorphism and dimorphism, with examples.

CHAPTER V.

1. What are the sources of heat, and what is the most probable view of its nature?

2. Give illustrations of the expansion of liquids and of solids by heat. What liquid forms a remarkable exception to the general law?

3. State the law according to which gases expand by heat. A certain volume of a gas measures 500 c.c. at 15° : what will be its volume at 288.2° ?

Ans. 1000 c.c.

4. A flask containing 2.4 litres is filled with a gas at 10° , and afterwards heated to 75° ; how much of the gas will escape?

Ans. 450 c.c.

5. Distinguish between *quantity* and *intensity* of heat. Which is measured by a thermometer?

6. Describe the method of constructing and graduating a thermometer.

7. The scale of a thermometer between the freezing and the boiling point was 1.5 metre in length. What will be the length of each division, (a) on the centigrade, (b) on the Fahrenheit scale?

Ans. (a) 15 mm., (b) $8\frac{1}{3}$ mm.

8. Ether boils at 95° Fahr.; mercury boils at 662° Fahr. Reduce these temperatures to the centigrade scale.

Ans. 35° C., 350° C.

9. Iodine melts at 107° C., and boils at 178° C. Reduce these temperatures to the Fahrenheit scale.

Ans. 224.6° F., 352.4° F.

Prove the correctness of the answers to the last two questions, by converting them back to Fahrenheit and centigrade respectively.

10. What is the unit of heat? How many units of heat are required to raise 560 c.c. of water from 0° to 42° ? *Ans.* 23.52.

11. Define specific heat. How may it be proved that different substances have different specific heats?

12. A kilogramme of mercury at 100° is mixed with 50 grms. of water at 20° ; what is the temperature of the mixture? *Ans.* 51.9° .

13. 1.5 kilog. of silver at 90° is agitated with 1 kilog. of water at 10° ; the temperature of the whole is found to be 16.4° . What is the specific heat of silver? * *Ans.* .057.

* The 1.5 kilog. of silver loses $(90 - 16.4 =) 73.6^{\circ}$. This is equivalent to $(1.5 \times 73.6 =) 110.4$ kilogs. losing 1° .

The kilogramme of water has gained 6.4° , or 6.4 units of heat; and this is sufficient to raise 110.4 kilogs. of silver through 1° . Hence the amount required to raise 1 kilog. of silver through 1° is $\left(\frac{6.4}{110.4} =\right)$.057 of a unit. A short statement of the rule is:

$$\frac{\text{Wt. of water} \times \text{its gain of temperature}}{\text{Wt. of substance} \times \text{its loss of temperature}} = \text{sp. heat of substance.}$$

14. State and explain Dulong and Petit's law connecting specific heats with atomic weights. Prove that it holds good for silver, iodine, gold, and mercury (for atomic weights see page 136).

15. Describe experiments which shew that all substances do not conduct heat equally well.

16. How is heat propagated through liquids and gases? Give experiments in illustration.

17. Explain what is meant by the radiation of heat. What connection is found to exist between the radiation and absorption of heat by the same substance?

18. What is 'latent heat,' and what explanation of it is given on the theory that heat is a mode of motion?

19. 1 kilogramme of water at 100° is mixed with the same weight of ice at 0° ; what will be the temperature of the liquid?

Ans. 10.5° .

20. Describe an experiment which proves that liquids, in becoming solids, evolve heat.

21. What is a freezing mixture? Explain the theory of its action.

22. Why does water, when steadily heated, pass only gradually into steam?

23. Steam at 100° is passed into 30 kilogrammes of water at 10° until the weight of the liquid is 31 kilogrammes. What will be the temperature of the liquid?

Ans. 29.9° .

24. Describe some methods of producing cold by evaporation.

25. In what different ways may a gas be liquefied? Give examples.

26. Describe the process of distillation. For what purposes is it used in chemistry?

CHAPTER VI.

1. What is believed to be the nature of light? How may the compound character of sunlight be demonstrated?

2. Describe the construction and use of a spectroscope.
3. What are Fraunhofer's lines, and what explanation is given of them?
4. Why is sodium believed to be present at the sun?
5. Describe, with a sketch, the spectra of calcium, lithium, rubidium, thallium.
6. What inferences are drawn from the examination of the light emitted from stars, planets, and nebulae respectively?
7. Give examples of the chemical action of light.

CHAPTER VII.

1. Describe an experiment illustrating the production of electricity by chemical action.
2. Explain the meaning of the terms quantity and intensity of a current.
3. Describe the galvanic batteries of Smee and Grove.
4. What is the probable nature of electrolysis, and what classification of elements has been founded upon its results?
5. Explain what is meant by an 'electro-chemical equivalent.'
6. Describe the process of electrotyping.
7. What chemical effects may be produced by the current of an electrical machine?

CHAPTER VIII.

1. What circumstances are found to modify chemical affinity?
2. Examine the characteristics of chemical combination as shewn by the union of oxygen and hydrogen. Give other examples of change of general appearance consequent on chemical combination.
3. Describe the mechanical separation of the constituents of gunpowder.
4. No weight is lost in chemical combination. How may this be shewn?

CHAPTER IX.

1. Write out a statement of each of the four laws of chemical combination, giving one illustration of each, and explaining its bearing on chemical work.
2. How may a table of combining proportions be constructed, and what unit or starting-point is generally adopted?

CHAPTER X.

1. What is the constitution of matter according to the atomic theory? Illustrate the answer by reference to oxygen and hydrogen.
2. Define 'molecule' and 'atom,' illustrating the difference in meaning of the terms.
3. Shew the bearing of the atomic theory on each of the laws of chemical combination.
4. What is a 'radicle?' Is it necessarily an isolable substance?

CHAPTER XI.

1. Describe the origin of some of the earlier chemical names. Is there any system observable in the nomenclature of the elements?
2. On what is the most modern system of nomenclature based?
3. What information is conveyed by the terms chloride, chlorite, chlorate; hyposulphite, sulphate; potassic sulphide, cuprous chloride, cupric sulphate; ferric nitrate; plumbic phosphate?
4. What is meant by an 'acid,' a 'base,' a 'salt,' an 'anhydride'?

CHAPTER XII.

1. Describe the construction of a series of chemical symbols for the elements, explaining exactly what the symbol represents.
2. How are formulæ constructed by the combination of

symbols? Distinguish between a rational and an empirical formula.

3. Give the meaning of the following symbols and formulæ :

H_2 . Na. SnO_2 . KCl. $Pb(NO_3)_2$. H_2Sb . $2(H_4N)_2SO_4$.

4. Give fully the information conveyed by the following equation :



CHAPTER XIII.

1. Distinguish between a gas and a vapour.

2. Describe an apparatus for the measurement of gases. What corrections are necessary in order to obtain the true volume of a gas comparable with the results of other observations?

3. The height of the barometer is said to be, on a particular day, 740 mm. What is meant by this statement?

4. Describe an apparatus for examining the effect of change of pressure upon the volume of a gas. What law is established by its employment?

5. 45 c.c. of carbonic dioxide were measured in a tube, when the barometer stood at 750 mm. The height of the column of mercury in the tube was 28 mm. Reduce the volume of the gas to standard pressure.

Ans. 43.34 c.c.

6. 15 c.c. of hydrogen are collected at 25° , under a pressure of 680 mm. What volume will the gas occupy at the standard pressure and temperature?

Ans. 12.293 c.c.

7. A glass globe holds 10 litres. If it is filled with oxygen at 0° , under a pressure of 760 mm., how much gas will escape when the temperature rises to 15° , and the barometer falls to 752 mm.?

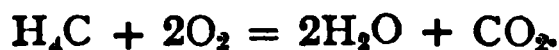
Ans. 661 c.c.

8. What is meant by the 'maximum tension' of a gas? By what different methods may a gas be liquefied? Give one example of the employment of each.

9. The density of carbonic dioxide is 1.529. Calculate the weight of 1 litre of the gas, and deduce from the result, by Ampère's law, the weight of a molecule of the substance.

10. How does Ampère's law account for the simple ratios in which gases combine by volume?

11. What results by volume are implied in the following equation?



CHAPTER XIV.

1. Give fully the steps by which we may ascertain the composition of the molecule of water.

2. Explain how we may determine the weight of the atom of an element which cannot be examined in the gaseous state.

3. What variations from the general law of atomic volume are presented by phosphorus, sulphur, and mercury respectively? How are these variations to be accounted for?

4. Give examples of the process of replacement in a compound substance, and shew how the idea of 'atomicity' has arisen from it.

5. Give examples of the principal classes into which radicles are divided according to their atomicity.

6. How have the apparent variations in atomicity of such a radicle as nitrogen been accounted for?

CHAPTER XV.

SECTION I.

1. What is the derivation of the name 'oxygen?' Mention some of the sources of the gas, and describe the process for preparing it which is usually employed in the laboratory.

2. Describe the construction and use of the pneumatic trough, and Pepys' gas-holder.

3. What weight of oxygen can be obtained from 100 grms. of potassic chlorate? *Ans.* 39.18 grms.

4. A gas-holder containing 50 litres is to be filled with oxygen at 0°. How much potassic chlorate must be taken for the purpose? *Ans.* 182.47 grms.

5. Describe experiments which illustrate the combustion of substances in oxygen, mentioning the characters of the compound formed in each case.
6. Into what main classes may oxides be divided?
7. Give a short account of what is known respecting ozone.
8. What are the sources of hydrogen in nature?
9. In what different ways may hydrogen gas be obtained from water?
10. Describe the usual process for preparing hydrogen, with a sketch of the apparatus.
11. Give experiments which illustrate the physical properties of hydrogen.
12. A rectangular india-rubber bag, 1 metre long, 50 cm. broad, and 30 cm. deep, is to be filled with hydrogen at 0° . How much zinc is required for the purpose? *Ans.* 428.5 grms.
13. The density of ordinary hydric sulphate is 1.84. How much hydrogen may be obtained by the action of zinc upon 20 c.c. of the acid? *Ans.* 8.38 litres.*
14. Describe the construction of an oxyhydrogen blow-pipe, and mention some of its effects.
15. What are the principal impurities in spring water, and to what is their presence due? How may water be freed from them?
16. Distinguish between an efflorescent and a deliquescent salt.

SECTION II.

1. What are the chief natural sources of nitrogen? and what is the most simple method of preparing it?
2. Into what classes may gases be divided in relation to combustion? To which of these does nitrogen belong?
3. What is the proportion of oxygen and nitrogen in air, (a) by volume, (b) by weight?

* From the statement of the density we learn that a certain bulk of the acid weighs 1.84 times as much as the same bulk of water. Now, 20 c.c. of water weigh 20 grms. Hence 20 c.c. of the acid will weigh $(20 \times 1.84 =)$ 36.8 grms.

4. What other substances besides these two are present in air? and how may their presence be detected and accounted for?

5. Explain the uses in the economy of nature of each of the constituents of air.

6. What circumstances have rendered it doubtful whether air is a mechanical mixture, or a chemical compound? Give reasons for considering it to be the former.

7. Describe an apparatus for the exact analysis of air by weight. Taking the composition of air by weight given in the text, calculate its exact composition by volume.*

8. How much air is required to furnish oxygen for the combustion of 8.4 c.c. of hydrogen? *Ans.* 20 c.c.

9. Describe experiments which illustrate the diffusion of gases, and state the law expressing the rate of diffusion.

10. The composition of air is found to be very nearly uniform throughout. Give reasons for this.

SECTION III.

1. Trace the steps by which ammonia is obtained from coal. How may the gas be collected in jars for examination?

2. Explain in words, and by a diagram, the nature of the decomposition of ammoniac chloride by calcic oxide.

3. By what characters may ammonia be recognised?

4. How may the composition of the molecule of ammonia be ascertained?

* We know that 1.430 grm. of oxygen occupy the space of 1 litre; we have only to calculate, therefore, how much space 22.94 grms. of oxygen will occupy. The volume of the nitrogen may be ascertained in the same way, and the results then stated as a percentage.

Or otherwise,

Let W represent the weight of a substance;

V represent the space it occupies (say, in cubic centimetres);

D represent the weight of a unit of volume (say, of 1 c.c.).

Then it is true that $W = VD$.

Whence $V = \frac{W}{D}$, and $D = \frac{W}{V}$.

So that, given any two of the quantities, the third can be found.

By the help of the above, a great number of problems relating to weight and volume may be solved.

5. 40 c.c. of ammonia gas are decomposed by the electric spark; how much oxygen will be required to combine with the hydrogen obtained? *Ans.* 30 c.c.

6. How may oxygen be caused to unite directly with nitrogen? Which oxide is produced?

7. What is the usual source of hydric nitrate, and what is the process for obtaining it?

8. Explain the chemical changes which occur in the preparation of hydric nitrate, shewing how they depend upon the temperature.

9. What weight of hydric nitrate is obtained by the decomposition, at a moderate temperature, of 30 grms. of potassic nitrate? *Ans.* 18.7 grms.

10. How much water must be added to 100 c.c. of ordinary hydric nitrate (density = 1.423), in order to reduce it to a density of 1.21? *Ans.* 150.2 c.c.

11. What is a 'test?' By what tests may a nitrate be detected?

12. What is the strength of the acid obtained by mixing ordinary hydric nitrate (density = 1.423) with an equal volume of water? *Ans.* 25.01 N₂O₅ per cent.

13. How is nitric peroxide obtained? What is the action of water upon the substance?

14. For what purposes is potassic nitrite used in the laboratory? How is the salt prepared?

15. Describe an experiment illustrating the direct oxidation of ammonia.

* See the table of densities (Table III.) at the end of the book. The acid, of which the density is 1.21, contains 29.48 per cent. of nitric anhydride; that is, 29.48 grms. of the anhydride with 70.52 grms. of water, or (by a simple proportion) 60.6 grms. of anhydride with 144.97 grms. of water.

The acid, of which the density is 1.423, contains 60.6 grms. of anhydride, with 39.4 grms. of water. We have, therefore, to add to each 100 grms. of the latter as much water as will make up the whole quantity associated with the anhydride to 144.97 grms., or (144.97 - 39.4 =) 105.57 grms. of water.

But 100 c.c. of acid of the density 1.423 weigh 142.3 grms. Hence from the proportion:

$$100 : 142.3 :: 105.57 : 150.2,$$

we learn that the 100 c.c. of strong acid must be mixed with 150.2 grms., or 150.2 c.c. of water, to obtain the weaker acid required.

16. Give fully the reaction which takes place when hydric nitrate acts upon copper, explaining the method by which it may be expressed in the form of an equation.

17. What points must be known or assumed before an equation can be constructed?

18. In what physical respects does nitric oxide differ from nitric peroxide?

19. Explain the formation of red vapours when nitric oxide is brought in contact with air. For what purpose is this reaction used?

20. Describe an experiment which shews that nitric oxide may be considered a supporter of combustion.

21. Give the steps by which nitrous oxide may be obtained from hydric nitrate.

22. What volume of nitrous oxide, and what weight of water, are obtained by the decomposition of 56 grms. of ammoniac nitrate?

Ans. 15.7 litres of gas; 25.2 grms. of water.

23. Give the properties in which nitrous oxide resembles oxygen. How may it be distinguished from oxygen?

24. What weight of nitrous oxide is required for the combustion of 6.7 litres of hydrogen, and what volume of nitrogen remains?

Ans. 13.2 grms. of gas; 6.7 litres.

25. Why has nitrous oxide been called 'laughing gas'?

26. Give a list of the oxides of nitrogen, with their chemical formulæ and composition by weight and volume. Compare shortly their physical properties.

SECTION IV.

1. Give some account of the different varieties of carbon, distinguishing between those which are, and those which are not, found in the mineral world.

2. What is meant by an 'allotropic' form?

3. For what purposes is animal charcoal employed?

4. What are the sources of carbonic dioxide, and from which of them is it generally obtained? Describe the preparation and mode of collection of the gas.

5. What volume of carbonic dioxide can be obtained from 20 grms. of marble? *Ans.* 4.47 litres.

6. What volume of air is required for the combustion of 3 grms. of carbon, and how much carbonic dioxide is produced? *Ans.* 28 litres of air; 5.5 litres of gas.

7. Illustrate the solubility of carbonic dioxide in water.

8. How has carbonic dioxide been liquefied and solidified?

9. What is the best test for the presence of carbonic dioxide, and how may its composition be ascertained?

10. Describe experiments which shew the sources of the carbonic dioxide in the air. Why does it not accumulate there?

11. How may carbonic oxide be obtained from carbonic dioxide?

12. How much oxygen is required to convert 3 grms. of carbon into carbonic oxide? *Ans.* 2.79 litres.

13. Describe the ordinary process for obtaining carbonic oxide.

14. How much oxygen is required for the complete combustion of the carbonic oxide obtained from 3 grms. of carbon, and how much carbonic dioxide is produced?

Ans. 2.79 litres; 5.58 litres.

15. What is a hydrocarbon? What are the chief hydrocarbons present in coal-gas?

16. What gas is produced when alcohol is heated with excess of strong hydric sulphate? Give the equation expressing the reaction.

17. How much oxygen is required for the combustion of 2.5 litres of ethylene, and how much carbonic dioxide is formed?

Ans. 7.5 litres; 5.0 litres.

18. Describe the results of acting upon ethylene with chlorine, stating the proportions by volume required of the latter.

19. What other substance has the same density as ethylene?

20. Two litres of ethylene are mixed with the same volume of marsh-gas. What volume of oxygen will be required for their complete combustion, and how much water and carbonic dioxide will be formed?

Ans. 10 litres of oxygen; 12.85 grms. of water; 6 litres of carbonic dioxide.

21. Describe the manufacture of coal-gas. What other products are obtained in the course of its preparation?
22. What is the cause of the violent explosion of fire-damp?
23. What is the construction of the Davy lamp? Describe experiments which shew the principle on which its safety depends.
24. Describe with a diagram the structure of the flame of a candle. Upon what does its luminosity depend?
25. What are (1) a Bunsen burner, and (2) a mouth blow-pipe? Describe experiments which illustrate the use of the latter.
26. How is cyanogen obtained? What is the composition, and what are the properties, of its compound with hydrogen?
27. How may the presence of a cyanide be detected?

SECTION V.

1. Describe one method of preparing chlorine, and state the precautions necessary in collecting the gas.
2. What volume of chlorine may be obtained by the action of manganic dioxide upon 60 c.c. of ordinary hydric chloride (density = 1.2)? *Ans.* 4.45 litres.
3. Describe experiments which illustrate the action of chlorine upon colouring matters and metals.
4. Why does a candle burn with a smoky flame when immersed in chlorine?
5. By what reactions may a chloride be detected?
6. Give the equation which represents the action of hydric sulphate upon common salt.
7. How may the action of hydric chloride upon ammonia be shewn?
8. How is the composition of hydric chloride accurately ascertained?
9. When aqua regia is made by mixing 3 measures of hydric chloride (density = 1.15) and one measure of hydric nitrate (density = 1.423), which acid is in excess?
10. Compare the list of chlorine oxides with that of the nitrogen oxides.

11. How is bleaching powder prepared? Mention some of its uses, as a source both of chlorine and of oxygen.

12. When chlorine is passed through a solution of potassic hydrate, what products are formed, (a) when the liquid is cold, (b) when it is heated?

13. What is the action of strong hydric sulphate upon a chlorate?

14. Describe the sources and preparation of bromine, and the physical properties of the element. What compounds does it form with oxygen?

15. How is iodine obtained from kelp?

16. Can hydric iodide be obtained in the same way as hydric chloride? What is the practical method of preparing the substance? How far does it resemble hydric chloride in properties?

17. What is the density of bromine vapour? Deduce from it the weight of the molecule of bromine.

18. A solution contains potassic chloride, iodide, or bromide; how may it be ascertained which of the three is present?

19. What is the most important compound of fluorine? How is it prepared, and what is its most valuable property?

20. When silicic fluoride is passed into water, what substances are produced?

SECTION VI.

1. How is sulphur obtained, and in what allotropic forms does it occur?

2. The vapour-density of sulphur at 500° is said to be anomalous. Explain this statement.

3. How is sulphurous anhydride prepared, and what are its properties? Why is it called an anhydride?

4. What is meant by a reducing agent? Describe experiments which shew the reducing action of hydric sulphite.

5. What is Nordhausen acid, and how is it obtained?

6. Can an atom of sulphur be made to unite directly with more than two atoms of oxygen?

7. Describe the English process for the manufacture of hydric sulphate.

8. How much hydric sulphate can be obtained from 1024 kilogrammes of sulphur? *Ans.* 3136 kilogrammes.

9. How much dilute hydric sulphate (density = 1.3) must be taken to neutralise 50 c.c. of a solution of ammonia of which the density is 0.9? *Ans.* 72.33 c.c.

10. How much water must be added to 30 c.c. of strong hydric sulphate in order to make a solution containing 40 per cent. of acid (H_2SO_4)? *Ans.* 83.07 c.c.

11. What classes of salts are derivable from hydric sulphate? Write out the formulæ of the ammonic salts in such a way as to shew their mutual relation.

12. How is sodic hyposulphite made, and for what purposes is it used?

13. Give experiments illustrating the use of hydric sulphide in the laboratory. To what extent is the gas soluble in water, and how is a solution of it prepared?

14. Give a short account of carbonic disulphide.

SECTION VII.

1. In what combinations does phosphorus occur, and how is it obtained?

2. How are lucifer matches made? In what respects is amorphous phosphorus better than ordinary phosphorus in their manufacture?

3. Describe the method of preparing hydric phosphide. What are the chief properties of the gas?

4. How many oxides of phosphorus are there, and how may they be obtained?

5. How much phosphorus must be taken to produce 46.86 grms. of phosphoric anhydride? *Ans.* 20.46 grms.

6. What is meant by the basicity of an acid? Give examples in illustration.

7. What salts are derivable from hydric orthophosphate, and by what tests may they be detected?

8. Describe the decomposition of 'microcosmic salt' by heat. What tests may be applied to the product formed?
9. Describe the compounds formed by phosphorus with chlorine.
10. In what compounds does boron occur in nature?
11. How is borax obtained, and for what blow-pipe tests is it used?
12. What is the action of hydric borate on test-paper?
13. Mention some of the natural sources of silicon. In what points does it resemble carbon?
14. What methods are there of decomposing silicates? In what combination is silicon thus obtained?
15. Describe the method of dialysis.
16. What is the composition of each of the chief varieties of glass? Explain why glass articles are very liable to crack, when heated or cooled suddenly.
17. How is silicic chloride obtained? From the results of its analysis, calculate the atomic weight of silicon.

CHAPTER XVI.

SECTION I.

1. Give the characteristics of a metal.
2. What metals are lighter than water, and which of them become liquid below the boiling-point of mercury?
3. Give illustrations of the malleability and ductility of the metals.
4. In what different ways may the oxide of a metal be obtained?
5. What are alloys? Give illustrations of the modified properties they exhibit.
6. Describe the character and occurrence of some metallic ores.
7. How may the metals be classified?

SECTION II.

1. How was potassium first prepared, and how is it manufactured? Describe experiments which illustrate its properties.
2. What is 'caustic potash,' and how is it obtained?
3. Calculate, from the equation given at page 355, the volume (at 0°) of carbonic dioxide and nitrogen given off during the explosion of 1 grm. of gunpowder. If the temperature is raised to 500° , how much will the volume be increased?
4. What is the process of testing for a potassic salt?
5. What are the natural sources of sodium? How far does the metal differ from potassium in properties?
6. Describe the process for the manufacture of common sodic carbonate.
7. How much crystallised sodic carbonate may be theoretically obtained from 100 kilogrammes of sodic chloride, and how much hydric sulphate (of the density 1.597) is required for the first stage of the process?
Ans. 244.4 kilogrammes, 74.92 litres of acid.
8. What are the tests for the presence of sodium?
9. Give a short account of rubidium and caesium.
10. For what reasons is it thought that the radicle ammonium may be a metal?
11. Mention the principal ammoniac salts, giving their formulæ, and comparing them with the corresponding potassic salts.
12. How may a solution be tested for ammonium?
13. Describe the process for obtaining silver from its ores.
14. How may pure silver be obtained on a small scale?
15. For what purposes is argentic nitrate used?
16. 100 grms. of silver yield 132.84 grms. of argentic chloride. If a molecule of the compound contains one atom of each of its constituents, and the weight of the chlorine atom is assumed to be 35.5, what is the atomic weight of silver?
17. Describe the collodion process in photography.
18. What are the tests for the presence of silver?

SECTION III.

1. Mention some minerals which contain calcium, strontium, and barium respectively.
2. What is meant by the 'slaking' of lime? How is mortar made, and what is the cause of its becoming hard?
3. Describe the methods of obtaining calcic, strontic, and baric oxides respectively.
4. What is Clark's process for rendering hard water soft?
5. What is plaster of Paris, and for what purposes is it used?
6. Give the chemical formulæ of Iceland spar, bone-earth phosphate, alabaster, dolomite, Epsom salts.
7. For what purposes are strontic salts chiefly used?
8. How is baric peroxide obtained, and how has it been employed as a source of oxygen?
9. Give the chief properties of hydric peroxide.
10. How is the metal magnesium obtained? Mention its properties and uses.
11. What difficulty is there in obtaining pure anhydrous magnesian chloride by evaporating its solution to dryness? How is this difficulty overcome?
12. How may we distinguish between a salt of barium, strontium, and magnesium, when present in a solution?
13. Baric sulphate is insoluble in acids. How may it be decomposed, and a soluble salt obtained from it?
14. A mineral is found to contain:

| | |
|-------------|-------|
| Zinc..... | 52.0 |
| Carbon..... | 9.6 |
| Oxygen..... | 38.4 |
| | <hr/> |
| | 100.0 |

What is the simplest formula representing its molecule?*

* If the atoms of all substances were of the same weight, then the results of analysis would of course represent directly the relative number of atoms in a molecule. But as atoms differ in weight, each of the above numbers must be divided by the atomic weight of the element, and the quotients reduced to their lowest terms, will (in the absence of other information, such as vapour density) give the formula of the molecule of the substance.

15. How is zinc obtained from its ores? What are its most important salts?

16. By what tests is zinc distinguished from magnesium and aluminium?

17. How is cadmium obtained? For what purposes are its salts used?

18. Describe the copper-smelting process as carried on at Swansea. To what ores is it applicable?

19. How is cupric oxide obtained? Describe experiments which illustrate its uses.

20. What is the formula of blue vitriol? Calculate the percentage of water in the salt.

21. What are the tests for the presence of copper?

22. From what sources is mercury obtained? Give the chief properties of the metal.

23. What is the density of mercury vapour? What inferences as to its molecular weight are drawn from it?

24. Give a table of the principal salts obtained from mercury, shewing the difference in their formulæ according to the atomic weight assigned to the element. State, shortly, the reactions by which they may be distinguished from each other.

25. How much mercuric chloride and mercurous chloride respectively may be obtained from 50 grms. of metallic mercury?

Ans. 67.75 grms. ; 58.875 grms.

26. Give an account of the process of lead-smelting. What is Pattinson's process of lead-refining?

27. What is the action of spring water and of rain water upon lead?

28. What is white lead, and how is it obtained?

29. Describe the oxides of lead, and the methods of obtaining them.

30. How may we detect the presence of lead in water?

SECTION IV.

1. Mention some of the sources of aluminium, and describe the method of obtaining the metal.

2. What is the constitution of alum, and how is it manufactured?
3. What is the meaning of a 'mordant' and a 'lake'?
4. How does common china differ from porcelain?
5. Calculate the percentage composition of crystallised alum.
6. Point out the analogies and differences between the elements aluminium, chromium, and manganese.
7. Illustrate the oxidation and reduction of substances from the series of chromium compounds.
8. Give the history of the element iron, and describe its chief ores.
9. Give details of the 'hot blast' smelting process.
10. Mention the difference in properties and composition between the principal varieties of iron and steel.
11. What is Bessemer's process for making steel?
12. 5 grms. of pure iron are burned (*a*) in oxygen, (*b*) in chlorine; what is the weight of the resulting compound in each case?
Ans. (*a*) 6.9 grms.; (*b*) 14.5 grms.
13. How are the ferrous and ferric salts distinguished from each other?
14. Give the points of difference between cobalt and nickel. In what respects do they both resemble iron?
15. Of what alloy is nickel an ingredient? For what purposes are the compounds of cobalt used?
16. What is the composition of pyrolusite?
17. How much oxygen, at standard pressure and temperature, can be obtained from 20 grms. of manganic dioxide, (*a*) by the action of heat; (*b*) by the action of hydric sulphate?
Ans. (*a*) 1.71 litres; (*b*) 2.57 litres.
18. How much chlorine can be obtained by the action of 20 grms. of manganic dioxide upon hydric chloride?
Ans. 5.143 litres.
19. What is the composition and formula of mineral chameleon, and from what property did it obtain its name?
20. How much iodine is set free by the action upon excess of (acidified solution of) potassic iodide of 5 c.c. of a solution

of potassic permanganate, containing 15.8 grms. of the salt in a litre?

Ans. 0.3175 grm.

21. Give an account of the occurrence of gold in nature.
22. How is gold leaf obtained? What is the composition of the alloy of gold used for coinage?
23. Describe the most important salt of gold, shewing how metallic gold may be obtained from it.
24. Give a short account of thallium, pointing out its analogies to lead and potassium.

SECTION V.

1. In what mineral does tin occur, and where is it found?
2. Describe the properties and uses of metallic tin.
3. How is stannic oxide obtained? What is the action upon stannic hydrate of an acid and an alkali respectively?
4. What are the tests for tin, and how may it be ascertained whether a stannous or a stannic salt is present?
5. How may pure metallic platinum be obtained in a compact form?
6. Describe experiments which illustrate the peculiar properties of finely divided platinum. What other metal possesses a similar property of absorbing gases?

SECTION VI.

1. Give the properties of the element bismuth. What two series of compounds does it form? By what tests is its presence recognised?
2. Mention the chief minerals which contain arsenic.
3. What is believed to be the weight of the molecule of arsenic? Give reasons for your answer.
4. What is the action of hydric nitrate upon bismuth, arsenic, and antimony respectively?
5. Describe Reinsch's test for arsenic. In what other ways may arsenic be reduced from its compounds?
6. Give an account of Marsh's test for arsenic, stating what substances interfere with its delicacy.

7. How is metallic antimony obtained from its ores? Compare its properties with those of bismuth and tin.
8. What compounds does antimony form with chlorine, and in what way are they decomposed by water?
9. What is the composition of tartar emetic?
10. How may Marsh's test be used to detect antimony, and to distinguish it from arsenic?
11. What other tests are there for the presence of antimony?
12. Give an account of the analogies of the group of elements to which antimony and phosphorus belong.

TABLE I.—COMPARISON OF THE METRICAL WITH THE COMMON ENGLISH MEASURES.

From tables arranged by WARREN DE LA RUE, F.R.S.

By Act of Parliament (27 and 28 Vict. cap. 117, 29th July 1864) the use of the Metrical System of Weights and Measures is rendered legal.
The weight of the Kilogramme is settled by this Act to be equal to 15432·3488 English grains.

| MEASURES OF LENGTH | In English Inches. | In English Feet = 12 Inches. | In English Yards = 3 Feet. | In English Fathoms = 6 Feet. | In English Miles = 1760 Yards. |
|--|-------------------------|--|--|--|--|
| Millimetre..... | 0·03937 | 0·0032809 | 0·0010936 | 0·0005468 | 0·0000006 |
| Centimetre..... | 0·39371 | 0·0328090 | 0·0109363 | 0·0054682 | 0·0000062 |
| Decimetre..... | 3·93708 | 0·3280899 | 0·1093633 | 0·0546816 | 0·0000621 |
| Metre | 39·37079 | 3·2808992 | 1·0936331 | 0·5468165 | 0·0006214 |
| Decametre..... | 393·70790 | 32·8089920 | 10·9363310 | 5·4681655 | 0·0062138 |
| Hectometre..... | 3937·07900 | 328·0899200 | 109·3633100 | 54·6816550 | 0·0621382 |
| Kilometre | 39370·79000 | 3280·8992000 | 1093·6331000 | 546·8165500 | 0·6213824 |
| Myriometre..... | 393707·90000 | 32808·9920000 | 10936·3310000 | 5468·1655000 | 6·2138244 |
| 1 Inch = 2·539954 Centimetres. 1 Foot = 3·0479449 Decimetres. 1 Yard = 0·91438348 Metre. 1 Mile = 1·6093149 Kilometre. | | | | | |
| MEASURES OF SURFACE | In English Square Feet. | In English Sq. Yards = 9 Square Feet. | In English Poles = 272·25 Sq. Feet. | In English Roods = 10,890 Sq. Feet. | In English Acres = 43,560 Sq. Feet. |
| Centiare, or sq. metre..... | 10·7642993 | 1·1960333 | 0·0395383 | 0·000988457 | 0·0002471143 |
| Are, or 100 sq. metres..... | 1076·4299342 | 119·6033260 | 3·9538290 | 0·098845724 | 0·0247114310 |
| Hectare, or 10,000 sq. metres... | 107642·9934183 | 11960·3326020 | 395·3828959 | 9·884572398 | 2·4711430996 |
| 1 Square Inch = 6·4513669 Square Centimetres. 1 Square Foot = 9·2899683 Square Decimetres. 1 Square Yard = 0·83609715 Square Metre or Centiare. 1 Mile = 0·404671021 Hectare. | | | | | |

TABLE II.
RELATION OF THE SCALES OF THE CENTIGRADE AND
FAHRENHEIT THERMOMETERS.

| Cent. | Fahr. | Cent. | Fahr. | Cent. | Fahr. | Cent. | Fahr. |
|---------------|-------|----------------|-------|---------------|-------|--------------|-------|
| + 100 = + 212 | | + 64 = + 147.2 | | + 29 = + 84.2 | | - 6 = + 21.2 | |
| 99 = 210.2 | | 63 = 145.4 | | 28 = 82.4 | | 7 = 19.4 | |
| 98 = 208.4 | | 62 = 143.6 | | 27 = 80.6 | | 8 = 17.6 | |
| 97 = 206.6 | | 61 = 141.8 | | 26 = 78.8 | | 9 = 15.8 | |
| 96 = 204.8 | | 60 = 140 | | 25 = 77 | | 10 = 14 | |
| 95 = 203 | | 59 = 138.2 | | 24 = 75.2 | | 11 = 12.2 | |
| 94 = 201.2 | | 58 = 136.4 | | 23 = 73.4 | | 12 = 10.4 | |
| 93 = 199.4 | | 57 = 134.6 | | 22 = 71.6 | | 13 = 8.6 | |
| 92 = 197.6 | | 56 = 132.8 | | 21 = 69.8 | | 14 = 6.8 | |
| 91 = 195.8 | | 55 = 131 | | 20 = 68 | | 15 = 5 | |
| 90 = 194 | | 54 = 129.2 | | 19 = 66.2 | | 16 = 3.2 | |
| 89 = 192.2 | | 53 = 127.4 | | 18 = 64.4 | | 17 = 1.4 | |
| 88 = 190.4 | | 52 = 125.6 | | 17 = 62.6 | | 18 = - 0.4 | |
| 87 = 188.6 | | 51 = 123.8 | | 16 = 60.8 | | 19 = 2.2 | |
| 86 = 186.8 | | 50 = 122 | | 15 = 59 | | 20 = 4 | |
| 85 = 185 | | 49 = 120.2 | | 14 = 57.2 | | 21 = 5.8 | |
| 84 = 183.2 | | 48 = 118.4 | | 13 = 55.4 | | 22 = 7.6 | |
| 83 = 181.4 | | 47 = 116.6 | | 12 = 53.6 | | 23 = 9.4 | |
| 82 = 179.6 | | 46 = 114.8 | | 11 = 51.8 | | 24 = 11.2 | |
| 81 = 177.8 | | 45 = 113 | | 10 = 50 | | 25 = 13 | |
| 80 = 176 | | 44 = 111.2 | | 9 = 48.2 | | 26 = 14.8 | |
| 79 = 174.2 | | 43 = 109.4 | | 8 = 46.4 | | 27 = 16.6 | |
| 78 = 172.4 | | 42 = 107.6 | | 7 = 44.6 | | 28 = 18.4 | |
| 77 = 170.6 | | 41 = 105.8 | | 6 = 42.8 | | 29 = 20.2 | |
| 76 = 168.8 | | 40 = 104 | | 5 = 41 | | 30 = 22 | |
| 75 = 167 | | 39 = 102.2 | | 4 = 39.2 | | 31 = 23.8 | |
| 74 = 165.2 | | 38 = 100.4 | | 3 = 37.4 | | 32 = 25.6 | |
| 73 = 163.4 | | 37 = 98.6 | | 2 = 35.6 | | 33 = 27.4 | |
| 72 = 161.6 | | 36 = 96.8 | | 1 = 33.8 | | 34 = 29.2 | |
| 71 = 159.8 | | 35 = 95 | | 0 = 32 | | 35 = 31 | |
| 70 = 158 | | 34 = 93.2 | | - 1 = 30.2 | | 36 = 32.8 | |
| 69 = 156.2 | | 33 = 91.4 | | 2 = 28.4 | | 37 = 34.6 | |
| 68 = 154.4 | | 32 = 89.6 | | 3 = 26.6 | | 38 = 36.4 | |
| 67 = 152.6 | | 31 = 87.8 | | 4 = 24.8 | | 39 = 38.2 | |
| 66 = 150.8 | | 30 = 86 | | 5 = 23 | | 40 = 40 | |
| 65 = 149 | | | | | | | |

TABLE III.—SPECIFIC GRAVITIES OR DENSITIES.

(A.) SOLIDS.

(For the Densities of the Metals, see page 339.)

Water at 4° = 1.000.

| | | | |
|------------------------|------|------------------|------|
| Phosphorus..... | 1.77 | Oak..... | 0.84 |
| Sulphur..... | 2.05 | Melting ice..... | 0.93 |
| Carbon (graphite)..... | 2.50 | Amber..... | 1.08 |
| " diamond..... | 3.51 | Ivory..... | 1.91 |
| Selenium..... | 4.30 | Porcelain..... | 2.38 |
| Iodine..... | 4.95 | Quartz..... | 2.65 |
| Cork..... | 0.29 | Marble'..... | 2.83 |
| Deal..... | 0.66 | Flint-glass..... | 3.33 |

(B.) LIQUIDS.

Water at 4° = 1.000.

| | | | |
|-----------------|-------|------------------------|-------|
| Ether..... | 0.715 | Water at 0°..... | 0.999 |
| Alcohol..... | 0.792 | Carbon disulphide..... | 1.263 |
| Turpentine..... | 0.869 | Bromine..... | 2.966 |
| Olive Oil..... | 0.915 | | |

(C.) GASES.

Air at 0° = 1.000.

| | | | |
|-----------------------|--------|---------------------------|--------|
| Hydrogen..... | 0.0693 | Carbonic Dioxide..... | 1.529 |
| Marsh-gas..... | 0.555 | Sulphur, at 600°..... | 6.62 |
| Ammonia..... | 0.596 | " at 1000°..... | 2.21 |
| Steam..... | 0.622 | Sulphurous Anhydride..... | 2.234 |
| Carbonic Oxide..... | 0.967 | Chlorine..... | 2.470 |
| Nitrogen..... | 0.971 | Phosphorus..... | 4.420 |
| Ethylene..... | 0.979 | Bromine..... | 5.540 |
| Nitric Oxide..... | 1.039 | Mercury..... | 6.976 |
| Oxygen..... | 1.106 | Iodine..... | 8.716 |
| Hydric Phosphide..... | 1.214 | Arsenic..... | 10.600 |
| " Sulphide..... | 1.191 | Alcohol..... | 1.610 |
| " Chloride..... | 1.247 | Ether..... | 2.586 |
| Nitrous Oxide..... | 1.520 | Carbonic Disulphide..... | 2.644 |

[The above are the results of experiment, and differ slightly in some instances from the densities given in the text, which are from Bunsen's *Gasometry*.]

TABLE IV.

Shewing the quantity of Sulphuric Anhydride (SO_2) and Hydric Sulphate (H_2SO_4) in Acid of different densities, at 15.5° (URE).

To find percentage of SO_4 , multiply the numbers in the second column by 1.2.

| Density of Solution. | Sulphuric Anhydride, SO_2 , in 100 parts by weight. | Hydric Sulphate (Oil of Vitriol), H_2SO_4 , in 100 parts by weight. | Density of Solution. | Sulphuric Anhydride, SO_2 , in 100 parts by weight. | Hydric Sulphate (Oil of Vitriol), H_2SO_4 , in 100 parts by weight. |
|----------------------|--|---|----------------------|--|---|
| 1.8460 | 81.54 | 100 | 1.3697 | 39.14 | 48 |
| 1.8415 | 79.90 | 98 | 1.3530 | 37.51 | 46 |
| 1.8366 | 78.28 | 96 | 1.3345 | 35.88 | 44 |
| 1.8288 | 76.65 | 94 | 1.3165 | 34.25 | 42 |
| 1.8181 | 75.02 | 92 | 1.2999 | 32.61 | 40 |
| 1.8070 | 73.39 | 90 | 1.2826 | 30.98 | 38 |
| 1.7901 | 71.75 | 88 | 1.2654 | 29.35 | 36 |
| 1.7728 | 70.12 | 86 | 1.2490 | 27.72 | 34 |
| 1.7540 | 68.49 | 84 | 1.2334 | 26.09 | 32 |
| 1.7315 | 66.86 | 82 | 1.2184 | 24.46 | 30 |
| 1.7080 | 65.23 | 80 | 1.2032 | 22.83 | 28 |
| 1.6860 | 63.60 | 78 | 1.1876 | 21.20 | 26 |
| 1.6624 | 61.97 | 76 | 1.1706 | 19.57 | 24 |
| 1.6415 | 60.34 | 74 | 1.1549 | 17.94 | 22 |
| 1.6204 | 58.71 | 72 | 1.1410 | 16.31 | 20 |
| 1.5975 | 57.08 | 70 | 1.1246 | 14.68 | 18 |
| 1.5760 | 55.45 | 68 | 1.1090 | 13.05 | 16 |
| 1.5503 | 53.82 | 66 | 1.0953 | 11.41 | 14 |
| 1.5280 | 52.18 | 64 | 1.0809 | 9.78 | 12 |
| 1.5066 | 50.55 | 62 | 1.0682 | 8.15 | 10 |
| 1.4860 | 48.92 | 60 | 1.0544 | 6.52 | 8 |
| 1.4660 | 47.29 | 58 | 1.0405 | 4.89 | 6 |
| 1.4460 | 45.66 | 56 | 1.0268 | 3.26 | 4 |
| 1.4265 | 44.03 | 54 | 1.0140 | 1.63 | 2 |
| 1.4073 | 42.40 | 52 | 1.0074 | 0.815 | 1 |
| 1.3884 | 40.77 | 50 | | | |

TABLE V.

Shewing the quantity of Nitric Anhydride (N_2O_5) in Liquid Hydric Nitrate (Nitric Acid) of different densities, at 15.5° (URE).

To find percentage of HNO_3 , multiply by 1.166.
" " NO_3 , " 1.148.

| Density of Solution. | N_2O_5 in 100 parts by weight. | Density of Solution. | N_2O_5 in 100 parts by weight. |
|----------------------|----------------------------------|----------------------|----------------------------------|
| 1.5000 | 79.700 | 1.2887 | 39.053 |
| 1.4940 | 77.303 | 1.2705 | 36.662 |
| 1.4850 | 74.918 | 1.2523 | 34.271 |
| 1.4760 | 72.527 | 1.2341 | 31.880 |
| 1.4670 | 70.136 | 1.2148 | 29.489 |
| 1.4570 | 67.745 | 1.1958 | 27.098 |
| 1.4460 | 65.354 | 1.1770 | 24.707 |
| 1.4346 | 62.963 | 1.1587 | 22.316 |
| 1.4228 | 60.572 | 1.1403 | 19.925 |
| 1.4107 | 58.181 | 1.1227 | 17.534 |
| 1.3978 | 55.790 | 1.1051 | 15.143 |
| 1.3833 | 53.399 | 1.0878 | 12.752 |
| 1.3681 | 51.068 | 1.0708 | 10.361 |
| 1.3529 | 48.617 | 1.0540 | 7.970 |
| 1.3376 | 46.226 | 1.0375 | 5.579 |
| 1.3216 | 43.835 | 1.0212 | 3.188 |
| 1.3056 | 41.444 | 1.0053 | 0.797 |

TABLE VI.

Shewing the quantity of Sodic Oxide (Na_2O) in solutions of Caustic Soda of various densities (DALTON).

To find percentage of sodic hydrate ($NaHO$), multiply by 1.29.
" " sodium (Na), multiply by 0.742.

| Density of Solution. | Sodic Oxide (Na_2O) in 100 parts by weight. | Density of Solution. | Sodic Oxide (Na_2O) in 100 parts by weight. |
|----------------------|---|----------------------|---|
| 1.56 | 41.2 | 1.32 | 23.0 |
| 1.50 | 36.8 | 1.29 | 19.0 |
| 1.47 | 34.0 | 1.23 | 16.0 |
| 1.44 | 31.0 | 1.18 | 13.0 |
| 1.40 | 29.0 | 1.12 | 9.0 |
| 1.36 | 26.0 | 1.06 | 4.7 |

TABLE VII.

Shewing the quantity of Hydric Chloride (HCl) in Liquid Acid (Hydrochloric Acid) of various densities, at 25° (E. DAVY).

To find percentage of chlorine (Cl), multiply by 0.97.

| Density of Solution. | Hydric Chloride in 100 parts by weight. | Density of Solution. | Hydric Chloride in 100 parts by weight. |
|----------------------|---|----------------------|---|
| 1.21 | 42.43 | 1.10 | 20.20 |
| 1.20 | 40.40 | 1.09 | 18.18 |
| 1.19 | 38.38 | 1.08 | 16.16 |
| 1.18 | 36.36 | 1.07 | 14.14 |
| 1.17 | 34.34 | 1.06 | 12.12 |
| 1.16 | 32.32 | 1.05 | 10.10 |
| 1.15 | 30.30 | 1.04 | 8.08 |
| 1.14 | 28.28 | 1.03 | 6.06 |
| 1.13 | 26.26 | 1.02 | 4.04 |
| 1.12 | 24.24 | 1.01 | 2.02 |
| 1.11 | 22.22 | | |

TABLE VIII.

Shewing the quantity of Potassic Oxide (K₂O) in solutions of Caustic Potash of various densities (DALTON).

To find percentage of potassic hydrate (KHO), multiply by 1.19.
" " potassium (K), multiply by 0.83.

| Density. | Potassic Oxide (K ₂ O) in 100 parts by weight. | Density. | Potassic Oxide (K ₂ O) in 100 parts by weight. |
|----------|---|----------|---|
| 1.60 | 46.7 | 1.33 | 26.3 |
| 1.52 | 42.9 | 1.28 | 23.4 |
| 1.47 | 39.6 | 1.23 | 19.5 |
| 1.44 | 36.8 | 1.19 | 16.2 |
| 1.42 | 34.4 | 1.15 | 13.0 |
| 1.39 | 32.4 | 1.11 | 9.5 |
| 1.36 | 29.4 | 1.06 | 4.7 |

TABLE IX.

Shewing the quantity of Ammonia (H_3N) in solutions of Ammonia of different densities, at 14° (CARIUS).

To find percentage of ammonium (H_4N), multiply by 1.089.

| Density of Solution. | Ammonia in 100 parts by weight. | Density of Solution. | Ammonia in 100 parts by weight. |
|----------------------|---------------------------------|----------------------|---------------------------------|
| 0.8844 | 36 | 0.9314 | 18 |
| 0.8864 | 35 | 0.9347 | 17 |
| 0.8885 | 34 | 0.9380 | 16 |
| 0.8907 | 33 | 0.9414 | 15 |
| 0.8929 | 32 | 0.9449 | 14 |
| 0.8953 | 31 | 0.9484 | 13 |
| 0.8976 | 30 | 0.9520 | 12 |
| 0.9001 | 29 | 0.9556 | 11 |
| 0.9026 | 28 | 0.9593 | 10 |
| 0.9052 | 27 | 0.9631 | 9 |
| 0.9078 | 26 | 0.9670 | 8 |
| 0.9106 | 25 | 0.9709 | 7 |
| 0.9133 | 24 | 0.9749 | 6 |
| 0.9162 | 23 | 0.9790 | 5 |
| 0.9191 | 22 | 0.9831 | 4 |
| 0.9221 | 21 | 0.9873 | 3 |
| 0.9251 | 20 | 0.9915 | 2 |
| 0.9283 | 19 | 0.9959 | 1 |

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